VOL. XXI. 1912

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

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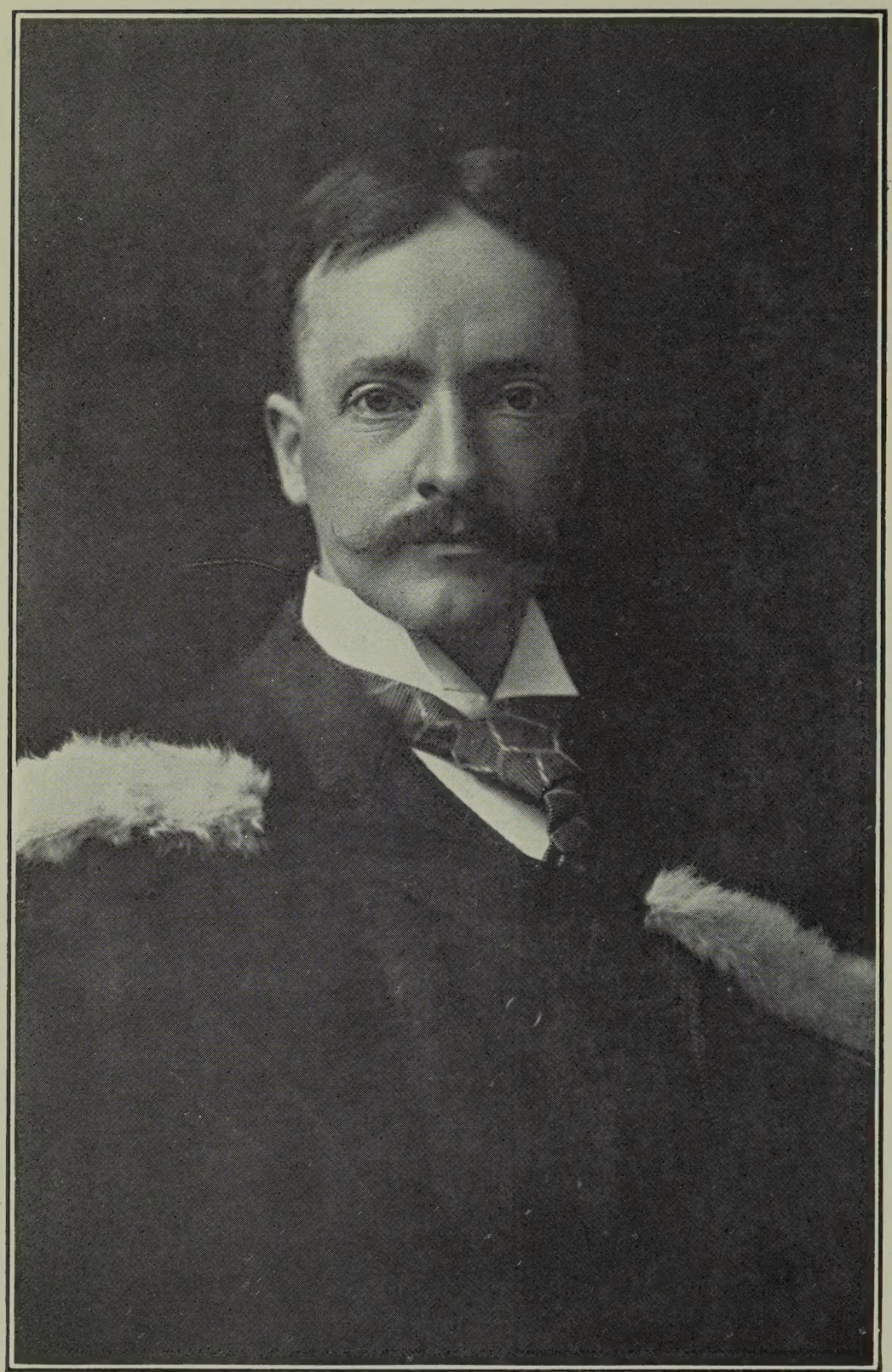

W. Lash Miller

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TRANSACTIONS

OF THE

AMERICAN

ELECTROCHEMICAL SOCIETY

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VOLUME XXI

TWENTY-FIRST GENERAL MEETING

BOSTON, MASS., APRIL 18, 19, 20, 1912

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.
1912

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VOLUME XXI. 1912.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-FIRST GENERAL MEETING OF THE SOCIETY, HELD IN BOSTON, MASS., APRIL 18, 19, 20, 1912.

Number of members registered, 102; guests, 67; total, 169.

PROCEEDINGS OF WEDNESDAY, APRIL 17th.

The Board of Directors met at 8.30 P. M. at the Hotel Lenox. The annual report of the Secretary and Treasurer made at that meeting and other actions there taken will be found printed at the end of these Proceedings.

PROCEEDINGS OF THURSDAY, APRIL 18th.

The Annual Business Meeting of the Society was called to order at 9.30 A. M. in the Chemical Lecture Room of the Lowell Building, Massachusetts Institute of Technology, Dr. W. R. Whitney, President, in the Chair.

The reading of the Minutes of the Twentieth General Meeting was dispensed with, and they were approved as published in the Transactions, Volume XX.

The report of the Board of Directors, including those of the Secretary and Treasurer, was read by the Secretary and accepted for publication in the proceedings of the meeting, to which it is appended.

In brief, the above reports show a total membership of 1,321 at the close of 1911, a net gain of 110 during that year. The

financial report shows a surplus of receipts above expenses of $1,299.60 during 1911, of which $1,040.00 was added to permanent investment account. The net assets of the Society at the close of 1911 were: Cash on hand, $1,276.73; Permanent Investment, $4,588.61; total, $5,865.34.

The Secretary reported the total membership at date of the meeting, including 15 members elected but not qualified, as 1,377, and the present net assets as $7,836.41.

The Secretary also reported that at the meeting of the Board of Directors held the evening previous it was voted that a sum not exceeding $250.00 be placed at the disposal of a Committee of three, to be appointed by the President, to be used for Assisted Research Work during the year of 1912-1913 (said Committee has been constituted as follows: Dr. W. R. Whitney, chairman; Mr. F. A. J. FitzGerald and Dr. Wm. H. Walker).

An amendment to the Constitution, which had been presented in proper form by the following members, P. McN. Bennie, F. M. Becket, H. R. Carveth, L. E. Saunders, Walter Wallace, Jos. W. Richards, F. A. Lidbury, E. M. Sergeant, Francis A. J. FitzGerald, R. C. Snowdon, William F. Meredith and Grant C. Moyer, printed in the bulletin and notice thereof thus sent to all members, was then taken up and passed. The said amendment is as follows:

"The Secretary shall send to all members nomination blanks not later than the 15th of December, and nominations upon these forms will be received by the Secretary not later than the 15th of January. He shall mail to every member before February 16th a printed list of all candidates thus nominated who have received more than 5 percent of the number of valid nominating ballots cast; he shall previously, however, give to each of such candidates notification of his nomination, within a week of which notification a candidate may elect to withdraw his name from the voting ballot. The voting need not be restricted to the names on the list. The Board of Directors may endorse those which it prefers, and, if so, the published list shall state it. Both nomination and voting shall be by secret letter ballot; the voter shall sign his name on an outside envelope, and the ballot shall be enclosed in an inner sealed and unmarked envelope. Voting ballots must reach the Secretary before the 16th day of March. The results of the

election shall be announced at the annual meeting." (In the discussion preceding this amendment the point was raised as to what should constitute "notification of nomination," and the amendment was passed with the general understanding that it included simply notice from the Secretary that the name had been placed in nomination.)

The report of the annual election for president, three vice-presidents, three managers, treasurer and secretary was then, in the absence of the tellers, opened by the Secretary and read as follows:

REPORT OF THE TELLERS OF ELECTION.

To the American Electrochemical Society:

GENTLEMEN: Following is the result of the count of ballots for officers of the American Electrochemical Society:

For President: W. Lash Miller 191, C. A. Doremus 101, L. Kahlenberg 20, W. R. Whitney 1, A. von Isakovics 1.

For Vice-Presidents: F. A. Lidbury 235, E. R. Taylor 224, L. H. Baekeland 104, Wm. Brady 94, W. Lash Miller 85, J. W. Brown 62, F. J. Tone 57, L. E. Saunders 2, S. S. Sadtler 1, C. A. Doremus 1.

For Managers: E. F. Roeber 276, L. E. Saunders 188, L. Kahlenberg 124, S. S. Sadtler 99, L. H. Baekeland 96, C. Baskerville 45, C. G. Schluederberg 44, H. R. Carveth 2, M. deK. Thompson 1, S. W. Parr 1.

For Treasurer: Pedro G. Salom 292.

For Secretary: Jos. W. Richards 295, W. S. Landis 1.

Respectfully submitted,

B. MACNUTT, *Chairman.*
S. S. SEYFERT,
W. S. LANDIS.

South Bethlehem, Pa.,
March 23, 1912.

The Chairman then announced that, in accordance with the report of the Tellers, he declared as elected the following:

President (for one year): W. Lash Miller.

Vice-Presidents (for two years): F. A. Lidbury, E. R. Taylor, L. H. Baekeland.

Managers (for three years): E. F. Roeber, L. E. Saunders, L. Kahlenberg.

Treasurer (for one year): Pedro G. Salom.

Secretary (for one year): Jos. W. Richards.

President W. R. Whitney noted his gratification at the large number of members participating in the election, also complimented the Society on its election of officers, and invited the President-elect, W. Lash Miller, to a seat upon the platform.

The business part of the session being concluded, the reading and discussion of papers were taken up as follows:

Papers were read by Carl Hering (2 papers), F. A. J. FitzGerald, C. P. Randolph, L. E. Saunders, R. Turnbull (presented by F. A. J. FitzGerald), Jos. W. Richards, J. Rattray Wilson, W. Sykes and T. F. Baily, and discussed, as printed in full in these Transactions.

The afternoon was occupied by alternative visits, first to the works of the General Electric Company at Lynn, visiting the River Works and the West Lynn Works; second, an excursion to Worcester, visiting first the works of the Norton Company, manufacturers of abrasive materials and refractory products, and next the Open-Hearth Department of the South Works of the American Steel and Wire Company, where the 15-ton Héroult electric furnace was seen in operation. Over 100 members and guests took part in these excursions.

On the evening of April 18th Prof. Chas. R. Cross, Professor of Physics at the Massachusetts Institute of Technology, gave an illustrated lecture on "Demonstrations of Electrical Discharge in High Vacua," which was listened to with great attention by a large audience.

Immediately following Professor Cross' lecture, a complimentary smoker was given to the visiting members and guests by the local members of the Society, in the Assembly Room of the Technology Union.

PROCEEDINGS OF FRIDAY, APRIL 19th.

The meeting was called to order at 9.30 A. M. in the Chemical Lecture Room of the Lowell Building, Massachusetts Institute of Technology.

The Presidential Address was then delivered by the Retiring

President, W. R. Whitney, the address being intended as the introduction to the Symposium on Electric Conduction which followed the address, as printed in full in these Transactions.

The rest of the session was occupied by the Symposium on Electric Conduction, presented by thirteen specialists in various lines, in which were discussed various phases of electric conduction in solids, liquids and gases, accompanied by demonstrations and explanations. The following gentlemen took part in this Symposium, their contributions, with the discussions, being printed in full in these Transactions: Dr. D. K. Comstock, Dr. E. Weintraub, Prof. R. A. Millikan, Dr. O. W. Richardson, Mr. M. W. Franklin, Dr. H. M. Goodwin, Prof. P. G. Nutting, Mr. C. J. Davisson, Dr. Wm. C. Bray, Dr. C. A. Kraus, Prof. S. J. Lloyd, in person, and written communications from Prof. S. C. Lind, Dr. D. McIntosh and Dr. E. W. Washburn. After noon luncheon at the Technology Union the Symposium was continued and closed. Afterwards Mr. F. W. Robinson, of the Hanovia Chemical Manufacturing Company of Newark, N. J., demonstrated some new apparatus imported from Germany and sold in this country by Mr. Chas. Engelhard, of New York City. The apparatus included an electric combustion furnace for the determination of carbon in steel, a resistance pyrometer with the platinum resistor embedded in fused quartz, and a fused-quartz mercury-vapor lamp.

In the evening over 60 members and guests participated in an informal dinner at the Hotel Vendome, at which interesting speeches were made by Drs. Walker, Whitney, Miller, Richards, Bancroft, Millikan and Richardson, and some very agreeable hours passed in social intercourse.

PROCEEDINGS OF SATURDAY, APRIL 20th.

The morning session was called to order at 9.30 o'clock in Pierce Hall, Harvard University, Cambridge. Prof. T. W. Richards of Harvard welcomed the Society in the following informal but interesting remarks:

Prof. Theodore W. Richards: Gentlemen, we take very great pleasure in welcoming you all to Harvard. It has been a matter of great regret to us all that the University has not been in operation during your stay here—this is the recess period,

and nothing is going on. Practically all of us had made plans for a vacation just at this time, before we knew that we should have the honor of your presence here; as you can well imagine, we are obliged to plan somewhat far ahead.

Nevertheless, I am especially glad to be here this morning and welcome you; I wish I could have seen more of you. I want also to state it would give the members of the Chemistry Department great pleasure to see you this afternoon at any time between 2.30 and 4.30, if you care to visit us in our venerable institution, called Boylston Hall, in the southern part of the college yard. Many of you have been there before, but perhaps those may like to revive old memories. The others, who have never seen the ancient structure, may be interested to look upon a building constructed by Josiah Parsons Cooke sixty-five years ago—a building which, I am inclined to think, is perhaps now the oldest large chemical laboratory in actual operation in the world.

Before many years we trust that you may visit us again, and by that time we shall hope for the realization of our dream of better accommodation for chemistry, especially for electrochemistry, than there is at the present time. One of the new chemical buildings is already in progress; it has advanced as far as the beginning of the first story. You may be interested to see the foundations and early beginnings of the structure. The building will be devoted entirely to research, and electrochemical investigation will form a considerable part of the work to be carried on there. Those who desire to see the plans can see them this afternoon at Boylston Hall. Fortunately the money for this first building is entirely at hand.

You may be interested also in the larger plans for the provision of buildings for all the rest of our chemical work. Our idea is that, in spite of the greater expense of the erection of several buildings instead of one huge structure, there are many advantages which overbalance this disadvantage. In the first place, having the different branches of chemistry somewhat separated is advantageous to each, because their needs are different and sometimes conflicting. The greater wall-space provides additional air and light, and the additional freedom from danger of fire is an added advantage. On the other hand, the nearness of the buildings will promote solidarity. Many appliances will be used

only in one building, yet because the buildings are to be close together there will be an opportunity of securing from any of the buildings apparatus which is desired in any other building.

However, this is a story which I really did not mean to speak to you about today. It only came to my mind because I thought you might be interested in hearing how the ancient Boylston Hall will, perhaps, soon be superseded.

In conclusion, let me once more very warmly welcome you to Cambridge, and once more express my regrets that I have not been able to see more of you during your stay here. (Applause.)

Papers were then presented and discussed as follows, as printed in full in these Transactions:

Papers by C. G. Fink, Merle Randall; Report of Committee on Standard Methods for Testing Dry Cells, presented by Prof. Chas. F. Burgess; papers by Carl Hambuechen (presented by C. F. Burgess), W. Lash Miller, R. Beutner, F. C. Mathers and O. Ralph Overman (presented by C. G. Schluederberg), W. D. Bancroft, C. W. Bennett (2 papers), W. D. Bancroft, C. W. Bennett and D. S. Cole (presented by Mr. Bennett), W. F. Bleecker, O. P. Watts (presented by C. F. Burgess), A. R. Johnson and W. R. Woolrich (presented by C. F. Burgess).

Professor Bancroft then presented the following resolutions, which were seconded by Dr. Hering and unanimously passed:

The American Electrochemical Society records its appreciation of the kind co-operation of its friends in and around Boston in making successful its Twenty-first General Meeting, and in particular directs that letters of thanks be sent to:

The Authorities of the Massachusetts Institute of Technology,
The Authorities of Harvard University,
The General Electric Company,
The American Steel and Wire Company,
The Norton Company,
Prof. Chas. R. Cross,
The Ladies' Committee,
The Local Committee of the Society, for their valuable assistance and entertainment during this meeting.

President Miller then declared the Twenty-first General Meeting of the Society adjourned.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and the Treasurer for the year 1911, the former containing the detailed financial statement of receipts and expenditures.

The increase in the number of members was satisfactory, being 110 net during the year. The membership at date of this meeting is, in round numbers, 1,362, with 15 members elected but not qualified by payment of dues, so that the number of members at this date is practically 1,377.

The financial status of the Society during 1911 continued satisfactory. The excess of receipts above expenditures for the year was $1,299.60, from which the permanent investment fund was increased by the purchase of a $1,000, 5 percent interest-bearing bond costing $1,040. The equity of the Society in the five $1,000 bonds held at the close of 1911 (diminished by the $500 Ferro-Boron prize held in trust) was over $4,500.

The following are the more important actions taken by the Board of Directors during the past year:

On January 28th The Pennsylvania State College Section of the Society was authorized, to include members in residence at State College, Pa., and its immediate vicinity.

On February 25th the Board authorized the Secretary to distribute to all members of the Society the papers printed in advance of the meetings.

On April 6th Mr. C. O. Mailloux was appointed to represent the Society at the International Congress of Applied Electricity at Turin, Italy. A design of a Society Pin was approved, and the Secretary was authorized to purchase a quantity and sell them to members.

On October 27th Dr. C. A. Doremus was appointed representative of the Society on the Local Committee of the Association for the Prevention of Accidents. Mr. E. R. Taylor was appointed a delegate of the Society to attend a meeting of the New York State Waterways Association to be held in Buffalo.

W. R. WHITNEY, *President.*
J. W. RICHARDS, *Secretary.*

SECRETARY'S ANNUAL REPORT.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN:—In 1911 the Society held two General Meetings, one in New York City, April 6th-8th, at which the attendance was 212 members and 149 guests, total 361; the second in Toronto, Canada, September 21st-23d, at which the attendance was 82 members and 38 guests, total 120. At the Spring Meeting 29 papers were read; at the Autumn Meeting 20.

In 1911 there were issued and distributed to our members two Volumes of the Transactions—Volume XVIII, the Transactions of the Chicago Meeting of October 13-15, 1910, and Volume XIX, Transactions of the New York Meeting of April 6-8, 1911. These Volumes contain 293 and 390 pages respectively.

The Transactions of the Toronto Meeting on September 21-23, 1911, were issued as Volume XX on January 16, 1912; it contains 499 pages.

The edition of each of the 1911 Volumes was 1,500 copies bound in cloth for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper for distribution to the Faraday Society, and 500 copies sewed, ready for binding, to be kept in stock.

In the 20 Volumes now issued as the Transactions of the first decade of the Society's activity there are 502 communications, covering 7,313 pages.

Complete sets of these Transactions are still on hand, but the stock is diminishing rapidly, and Volume III, which is nearly exhausted, is sold, according to the action of the Board of Directors, at double price.

An Alphabetical Index of the first 20 Volumes has been prepared in the Secretary's office, and the Board of Directors has authorized its publication and distribution, cloth bound, *gratis* to all members of the Society. It is hoped to have this Index distributed before the issue of Volume XXI, and it is certain that it will very greatly increase to members the value of their Transactions.

The stock of Volumes on hand December 31, 1911, was as follows:

Volume	Bound in Cloth	Bound in Paper or stitched ready for binding	Total
I	200	12	212
II	217	0	217
III	132	0	132
IV	157	234	391
V	108	234	342
VI	125	239	364
VII	126	247	373
VIII	140	248	388
IX	141	275	416
X	149	257	406
XI	139	261	400
XII	151	266	417
XIII	162	219	381
XIV	271	253	524
XV	269	222	491
XVI	39	522	561
XVII	207	518	725
XVIII	220	519	739
XIX	147	533	680
Total			8,159

Condition of the Society in regard to Membership in 1911:

Members January 1, 1911		1,211
Elected and qualified as members in 1911		198
		1,409
Resignations in 1911	32	
Deaths	6	
Dropped for non-payment of dues	50	
	—	88
Members December 31, 1911		1,321
Net gain in membership in 1911		110

Financial Statement.

January 1, 1911 to December 31, 1911.

RECEIPTS.

Entrance fees		$ 985 00
Current dues		6,316 47
Sales of publications		1,509 74
Advertisements		440 05
Membership certificates		36 00
Sales of society pins		100 54
Interest on investments and bank deposits		218 30
		$9,606 10

EXPENDITURES.

Office printing		$ 657 85
Postage		1,091 00
Publications		3,756 05
Secretary, salary, including stenographer		871 92
Assistant Secretary, salary		300 00
Office expenses		428 00
Engrossing membership certificates		11 30
Appropriations to sections		150 00
Storage		40 75
Accrued interest on bond purchased		20 83
Expenses of meetings		453 80
Faraday Transactions, payment of extra copies		347 50
Commissions paid on advertisements		44 00
Membership pins		112 50
Conservation commission expense		21 00
		$8,306 50
Excess, receipts above expenditures		$1,299 60
Permanent investment	$1,040 00	
Gain in cash balance	259 60	
		$1,299 60

ASSETS, JANUARY 1, 1911.

Cash balance, January 1, 1911, on deposit		$ 967 13
Cash box		50 00
Bonds held by the Society (cost price)	$4,048 61	
Ferro-Boron prize, held in trust	500 00	
Equity of Society in above bonds		3,548 61
		$4,565 74

ASSETS, DECEMBER 31, 1911.

Cash balance, December 31, 1911, on deposit		$1,226 73
Cash box		50 00
Bonds held by the Society (cost price)	$5,088 61	
Ferro-Boron prize, held in trust	500 00	
Equity of Society in above bonds		4,588 61
		$5,865 34
Gain in assets for the year of 1911		$1,299 60

Jos. W. Richards,
Secretary.

TREASURER'S ANNUAL REPORT.

FOR THE YEAR 1911.

Balance, January 1, 1911	$ 1,017 13
Receipts from Jos. W. Richards, January 1, to December 31, 1911	9,606 10
	$10,623 23
Payments January 1, 1911, to December 31, 1911, as per list	$9,346 50
Balance December 31, 1911	$ 1,276 73

PEDRO G. SALOM,
Treasurer.

We have examined the accounts of the American Electrochemical Society, verified the receipts and expenditures submitted herewith, and find them correct.

(Signed) HENRY G. MORRIS,
S. S. SADTLER,
Auditors.

MINUTES OF MEETING OF THE BOARD OF DIRECTORS.

The meeting was held at the Hotel Lenox, Boston, Mass., on Wednesday, April 17th, at 8.30 P. M., the evening preceding the annual meeting of the Society.

Present in person: Whitney, Walker, Roeber, Sadtler, Fitz-Gerald, Isakovics, Taylor, Miller, Lidbury, Burgess, Hering, Salom, Richards; present by proxy: Baekeland, Kahlenberg, Smith, Tucker, Bancroft. The minutes of the meeting of March 23d were approved as printed.

The matter of corresponding with the Pacific Coast Borax Company regarding re-advertising the $500 Ferro-Boron prize, or making other disposition of the prize money now in the hands of the Society, was referred to the Executive Committee, with power to act in the premises.

Ordered that the limitation as to selling the last 100 copies of any volume of the Transactions only as parts of complete sets be removed.

The annual report of the Secretary was received and accepted.

The annual report of the Treasurer, properly certified by the auditors, was received and accepted. These reports will be printed in full in the Proceedings of the Twenty-first General Meeting, Volume XXI of the Transactions.

The Committee on "Dry Cell Tests" reported through Prof. Chas. F. Burgess that a preliminary report had been printed and distributed and would be called up for discussion at the sessions of the Society.

The Conservation Committee reported progress, through Mr. E. R. Taylor, who gave a short account of the Kansas City Meeting of the Conservation Congress.

Sundry "Rulings of the Board," called for at the last General Meeting of the Board, were submitted by the Secretary in type-written form; their consideration was deferred.

A motion by Mr. Salom that "a medal be awarded for the most meritorious paper presented to the Society by a member, and with it an appropriation of money up to $250, if thought desirable," was lost.

Mr. F. A. J. FitzGerald moved: That a sum not exceeding $250 be placed at the disposition of a committee of three, to be appointed by the President, to be applied to the furtherance of scientific experimental research during the year 1912-1913. The committee is to advertise this matter in the Bulletin, receive applications for such financial assistance, make grants to such member or members as it may select, and require the results of such assisted research to be presented in proper form to the Society. The motion was passed.

Proposed changes in the By-Laws offered by a committee appointed to consider means of bringing into effect the recommendation of the "Committee on the Improvement of Publications" were discussed at length and adopted in the following form:

Section 3, Paragraph 3:

Add at end of Paragraph 3: "It shall be the further duty of the Secretary to organize and maintain means for securing the submission of papers to the Publication Committee.

Section 4:

Delete Paragraph 1 relating to the "Committee on Papers."

Substitute the following for the paragraph relating to the Publication Committee:

"The Publication Committee shall consist of a Chairman, the President *(ex-officio)*, the Secretary *(ex-officio)* and four members. The Chairman of the Committee, to serve for one year, and two members, to serve for two years, shall be appointed yearly by the incoming President, subject to the approval of the Board of Directors. (In the first instance four members shall be appointed, two to serve for two years, and two to serve for one year.) Retiring members shall be eligible for reappointment. Vacancies arising on the Publication Committee shall be filled by appointment by the President, subject to the approval of the Board of Directors.

"The Publication Committee shall meet at each general meeting of the Society, at which time it shall set a date prior to which papers for the next meeting may be submitted. It shall pass on all papers so submitted, and shall have complete discretion as to what papers shall be accepted for presentation at the meetings of the Society; provided, however, that any member may appeal to the Board of Directors against any decision of the Committee with respect to a paper submitted by that member.

"The Committee shall deal with all papers submitted as promptly as possible, and shall, where desirable, assist authors by suggestions which would improve the form of their papers as submitted.

"No member of the Committee shall pass on any paper of his own.

"The Committee shall have charge of the publication of the Transactions of the Society, and shall decide what papers shall be published in the Transactions. The editing of the Transactions shall be in the hands of the Committee.

"The Committee may assign work in connection with its duties to whatever member of the Society it sees fit.

"The Chairman of the Publication Committee shall keep a record of all papers submitted and of the action taken thereon. He shall report to the Board of Directors at each general meeting of the Society, and shall be responsible to the Board for the carrying out of the Committee's duties according to the By-Laws.

Rulings of the Board.

"In general, no paper may be presented at a meeting of the Society unless it has been submitted, in full, prior to a date set by the Publication Committee as suitable to allow consideration by that Committee and the printing of advance copies before the meeting. In exceptional cases the President may authorize a paper, not previously submitted to the Publication Committee, to be read; such authorization will not, however, bind the Society or the Publication Committee in any way as to printing or publication.

"Papers of the following classes will be regarded as undesirable:

(a) Those containing no information or obviously incorrect information.

(b) Those containing only information already easily accessible.

(c) Those of an advertising nature not counterbalanced by adequate scientific information and treatment.

"Authors' abstracts of papers already published elsewhere may, however, be accepted for the purpose of discussion. Papers already published but not easily accessible will, if otherwise desirable, generally be accepted.

Advance Copies of Papers.

"Advance copies of such papers as are accepted by the Publication Committee will be printed as soon as possible for distribution before the meeting, and the author will receive twenty-five of these copies *gratis* and have the right to order as many as he may wish at the regular rates.

Discussions.

"The Publication Committee will edit discussions; it shall not, however, change the meaning of any contributor's remarks, and the revised form of each contributor's remarks will be sent to him for approval; unless objection be raised within one week, it will be assumed that such revision is approved."

Adjourned.

Joseph W. Richards,
Secretary.

MEMBERS AND GUESTS REGISTERED AT THE TWENTY-FIRST GENERAL MEETING.

Members.

Paul O. Abbe
R. Amberg
W. C. Arsem
T. F. Baily
W. D. Bancroft
F. M. Becket
C. W. Bennett
E. R. Berry
R. Beutner
W. F. Bleecker
P. A. Boeck
John C. Bradley
Wm. C. Bray
John W. Brown
N. W. Buch
C. F. Burgess
Chas. R. Cary
Chas. A. Catlin
Jesse Coates
F. P. Coffin
R. W. Davis
Chas. A. Doremus
L. H. Duschak
C. G. Fink
F. A. J. FitzGerald
Karl G. Frank
M. W. Franklin
Jas. J. Gerety
Arthur E. Gibbs
A. McK. Gifford
J. S. Goldbaum
H. M. Goodwin
M. L. Griffin
J. R. Griffith
C. A. Hansen
L. O. Hart
Carl Hering
H. D. Hibbard
A. C. Higgins
Alcan Hirsch
Chas. V. Holman
A. H. Hooker
Henry Howard
L. E. Howard
O. T. Hungerford
A. von Isakovics
D. C. Jackson
W. McA. Johnson
R. M. Keeney
M. M. Kohn
M. O. Lamar
F. A. Lidbury
S. J. Lloyd
Dorsey A. Lyon
P. R. Manahan
C. W. Marsh
A. C. Melcher
W. Lash Miller
T. A. Mitchell
J. M. Muir
C. H. Ohlwiler
Geo. S. Page
John C. Pennie
N. Petinot
W. B. Pritz
Merle Randall
Edward Quintard
Jos. W. Richards
T. W. Richards
E. F. Roeber
S. S. Sadtler
Pedro G. Salom
R. N. Sargent
L. E. Saunders
C. G. Schluederberg
John A. Seede
S. P. Sharples
Chas. E. Skinner
W. C. Slade
Wm. Acheson Smith
H. Clyde Snook
E. C. Sprague
John S. Stone
H. W. Sykes
H. P. Talbot
E. R. Taylor
B. F. Thomas
M. deK. Thompson
C. B. Thwing
C. P. Townsend
S. A. Tucker
M. Unger
Geo. D. van Arsdale
W. H. Walker
Louis E. Ward
E. Weintraub
A. Benj. Werby
W. R. Whitney
L. M. Willey
J. Rattray Wilson
W. J. Wooldridge
John A. Yunck

Guests.

Mrs. F. M. Becket
Mrs. F. A. J. FitzGerald
Miss M. E. Gibbs
Miss P. L. Gifford
Mrs. H. D. Hibbard
Mrs. A. von Isakovics
Miss M. von Isakovics
Mrs. G. S. Page
Mrs. E. Quintard
Mrs. W. E. Ruder
Mrs. J. A. Seede
Mrs. E. H. Taylor
Mrs. E. R. Taylor
Mrs. C. P. Townsend
Mrs. J. Rattray Wilson

Guests (Continued.)

C. L. Allen
Walter Arthur
A. N. Barron
E. H. Bedell
A. O. Beneomy
S. P. Bergman
A. A. Blanchard
L. C. Brown
J. H. Byrne
M. J. Callahan
W. A. Carter
A. L. Chesley
R. T. Childs
F. M. Claflin
T. E. Crossman
C. Davisson
C. W. Dietz
Boyd Dudley, Jr.
Jas. H. Ellis
Wm. R. Fleming
F. E. Gallagher
John B. Glaze
L. R. Gonzalez
J. S. Gravely
E. J. Gray
I. S. Hartman
M. W. Hedden
A. T. Hinckley
H. T. Kalmus
H. S. Knowlton
A. Laih
F. C. Langenberg
S. H. Lawton
R. P. MacPherson
R. D. Mailey
J. P. Mayfield
M. F. Merrill
R. A. Millikan
J. P. Minton
E. Mueller
Geo. J. Niebuhr
P. G. Nutting
L. G. Odell
Walter O. Patrick
H. D. Pease
F. W. Robinson
W. E. Ruder
Walter H. Sawyer
E. H. Taylor
L. E. Underwood
M. A. Williamson
E. P. Young

Members Elected and Qualified.

October, 1911—March, 1912.

October 27, 1911.

Robert De Luce, Dome, Ariz.
R. N. Sargent, Perth Amboy, N. J.
Frank H. Briggs, Elyria, O.
John G. Homan, Steubenville, O.
T. L. Kolkin, Vadheim, Sogn, Norway.
Paul Chateau, Vennesla pr. Christiania, Norway.
Jas. Jos. Gerety, Philadelphia.
Heinrich Goldschmidt, Christiania, Norway.
G. A. Julius, Woollahra, Sydney, N. S. W., Australia.
B. F. Lovelace, Baltimore, Md.
J. E. Schultzberg, Tyssedal, Hardanger, Norway.
J. Watson Bain, Toronto, Canada.
Nathaniel K. B. Patch, Toronto, Canada.
Edward McGall, Orange, N. J.

November 24, 1911.

Sigurd Giertsen, Odda, Norway.
Sokichi Murahashi, Osaka, Japan.
Ernst Gelbach, Hohenlohenhutte, O-S, Germany.
Herbert E. Rankin, Princeton, N. J.
Philip E. Kern, State College, Pa.
Emil Collett, Christiania, Norway.
Knud Bryn, Christiania, Norway.
D. H. Bradley, Jr., Parral, Chih., Mexico.
Floyd M. Skidgell, Orange, N. J.
Edward P. Fleming, Rancagua, Chile, S. America.
Robert M. Keeney, Golden, Col.
Chas. F. Pascoe, Montreal, Canada.

December 29, 1911.

Geo. F. Hughes, Bridgeport, Conn.
F. W. Cunningham, Point Pleasant, N. J.
Frederick R. Raeth, Milwaukee, Wis.

January 27, 1912.

Harold H. Smith, Orange, N. J.
James W. Owen, Camden, N. J.
Stafford Hill, Villa Nova de Lima, Minas Geraes, Brazil.
Edward G. Brownlee, Jr., Conneaut, O.
Philip K. Devers, Jr., West Lynn, Mass.
Otto K. Zwingenberger, Ph. D., Perth Amboy, N. J.
R. H. Pickens, Clemmons, N. C.
John Cook, M. E., Allendale, N. J.
J. T. Burt-Gerrans, Toronto, Ont., Canada.
Henry P. Armes, Winnipeg, Man., Canada.
Dr. Ing. A. Mueller, Oberhausen, Rhineland, Germany.
Dr. T. Hasegawa, Nikko, Japan.
Samuel N. Castle, New York City.

February 23, 1912.

Michaael Yatsevitch, Kiev, Russia.
Andrew Weisenburg, Philadelphia.
Ove Collett, Arendal, Norway.
John R. Griffith, Niagara Falls, N. Y.
Frederick W. Tilley, Davis, W. Va.
Louis P. Webert, Wilkinsburg, Pa.
Dr. Wilhelm Heraeus, Hanau, Germany.
James N. Lawrence, Madison, Wis.
Webster W. Benjamin, Hayden, Gila County, Ariz.
Augustus McK. Gifford, Pittsfield, Mass.
Louis Potthoff, Brooklyn, N. Y.
John H. Harris, Lockport, N. Y.

March 23, 1912.

William C. Brooks, Evansville, Ind.
Dr. Franz Fattinger, Treibach, Carinthia, Austria.
William Lord Bliss, Niagara Falls, N. Y.
A. Benjamin Werby, State College, Pa.
W. Harry Fenoughty, East St. Louis, Ill.
Dottor Carlo Rossi, Legnano, (Milan,) Italy.
Francis A. Jacobs, Montreal, Quebec, Canada.
Philip J. Brewer, London, England.
Mark O. Lamar, Schenectady, N. Y.
Charles W. Bennett, Ithaca, N. Y.
Charles P. Randolph, Great Barrington, Mass.
Joseph Adams Inslee, La Paz, Bolivia, South America.

The Presidential Address, introducing a Symposium on Electric Conduction, delivered at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912.

ELECTRICAL CONDUCTION.

By W. R. Whitney.

The symposium on electric conduction which will be held in connection with this meeting determines me to make this presidential address a part of, or rather an introduction to, this symposium. We are endeavoring to bring together in this session men who are actively at work studying different phases of electrical conduction, and many of us feel that we are in the midst of a period of great advance in our conceptions of electrical phenomena, and that knowledge gained in any of the separate fields, such as, for example, vacuum tubes, is becoming applicable to other parts, such as open-air arcs or even metals. "Ions" and "Electrons" are not the personal property of a small group of pure physicists, but are rapidly becoming the *alpha, beta* and *gamma* of electrochemistry in general. It is to help insure the common understanding of the fundamental conceptions of these things, that this subject was chosen for our symposium.

The illustrated lecture by Prof. Chas. R. Cross last evening, demonstrating so beautifully electrical discharges in high vacua, served as a splendid introduction to that part of the subject in which the greatest experimental yield has been obtained in the past few years. My own excuse for performing one single experiment is to prove my willingness to dare to call your attention to well-known and simple facts, and add a few to the number of phenomena which modern theories are co-ordinating.

No attempt is made to have this address set forth new discoveries, nor even to deal in an orderly way with old ones. It is rather intended to help recall, in simple manner, to the minds of those who already know them, a few of the facts of electrical conductivity. I am impressed with the thought that some of the simplest facts are often very interesting, and whatever ideas

or theories of conduction are advocated, they must first serve to cover and clothe such facts as I am considering.

The bare fact that electrical conductivity of pure metals increases with falling temperature at approximately the same rate for all the metals must be of the utmost importance to a further understanding of the phenomena of conductivity.

That the temperature coefficient of resistivity is about the same as that for the expansion of gases, undoubtedly led to the attempts to apply gas laws to the conducting ions in metals. Just as we cannot obtain gases of appreciably higher expansion coefficient than 0.0037 by any system of mixing them, so also we fail by alloying the metals to get any alloy having a higher resistance-coefficient than this value. Magnetic metals, such as iron and nickel, have a somewhat higher coefficient because of the inductive effect, but this irregularity is, we are told, in turn a support of the ionic theory of conduction.

The work of Dewar and Fleming in 1893 and of Onnes in 1911 has carried the range of exact determinations of electrical conductivity of metals to such low temperatures and such high conductivities that electrical resistances in some cases were not observable at all. For example, pure gold wire immersed in boiling helium gave Onnes no measurable resistance. (The helium itself shows no conductivity, which puts this element out of the class of metals.) At these exceedingly low temperatures mercury also apparently loses its resistivity. This checks up well with Dewar and Fleming's conclusions. In 1893, after measuring many pure metals and alloys at boiling-oxygen temperatures, they wrote: "The electrical specific resistance of all pure metals will probably vanish at the absolute zero of temperature."

The work of these authors also shows plainly that the resistance of *alloys* in general does not disappear at zero. This in turn is a second fundamental fact which new conduction-theories must cover. It is interesting to speculate on that peculiarity of metals which allows their resistance to disappear when taken singly to low temperature, but does not do so when the same metals are mixed.

To any one who has wanted to make use of high specific resistance in metals, it must have appeared strange that there seem to be no ductile poor-conductors. The pure metals, or

those pure elements which can be obtained in wire form, for example, all possess high conductivities comprised within a rather narrow zone. From copper and silver, taken as 100 per cent. conductivity, it seems impossible to get in any pure metal wire even as little as 1/20th of this value. By the use of alloys, higher specific resistances are easily obtained, but as yet the range seems quite narrow. No ductile alloy seems to have a resistance as great as 100 times that of copper.

Such facts may perfectly properly interest us in various ways. Let us say first, merely as an interesting scientific fact, a truth of Nature, in which we have a right to find pleasure, but let us also grant the pleasure to the engineer who finds his enjoyment in speculating on the possibilities which such a fact seems to him to open up. He first sees the transmission of power with maximum conservation, if any method of maintaining low-enough temperature is opened to him, and so we hear of schemes for cooling long distance transmission lines by liquid air. Possibly the *"summum bonum"* will not be realized, but it may not be out of the question to utilize such fundamentally important discoveries.

The regularities thus far found in the resistances of alloys may be briefly considered. Perhaps the generalizations published by Guertler in the Zeitschrift für anorganische Chemie are the simplest. As a first general approximation, the alloys of metal-pairs may be divided into two classes: those which exhibit conductivity at least approximately calculable from the conductivities of the components and those which do not. For example, any alloy of lead and tin conducts about as the two quantities of the components would if placed side by side. This applies to alloys between lead, tin, zinc and cadmium.

There is another class of alloys which at certain compositions are simple chemical compounds, such as Cu_2Sb, Cu_3Sn, etc. These have conductivities not apparently to be predicted at all from the conductivity of the components. This corresponds to the variation of melting-points of alloys which latter follow in some cases quite simple general rules, but which do not permit of prediction of the melting-point of a compound when one is formed between the two metals. For example, most antimony-aluminum alloys melt higher than either component. We are

more familiar with this regularity when one of the pair is markedly less metallic than the other; for instance, neither the conductivity nor melting-points of iron and sulphur compounds could be guessed from the corresponding properties of the components, nor would zinc and sulphur compounds yield to such analysis. We are in such cases much more apt to refer to the optical properties, and to expect the black and opaque substance to conduct, and the white or transparent one not. This qualitative criterion is again subject to modification, and at high temperatures many of the insulators conduct well.

Between the *compounds* of metals and either of the metals themselves, mixtures are possible whose conductivity will be like that of the simple mixtures of lead, tin, etc.; that is, they will be calculable from the volume-concentration of the two components, when the metal compound is considered as one component, and so also when two metals form two different compounds these two may act in turn like the single metals lead and tin. If this were all, then the laws of resistance of alloys would be quite simple. There is another feature which involves the crystallization-condition of the alloys on cooling from a molten state. In the case of the lead-tin or the simple group, the metals crystallize out pure, just as salt or ice may separate from an aqueous solution, but in other cases the freezing microscopic crystal is itself a mixture and the composition may change with the liquid concentrations, so that the resistance of the final solid is no longer calculable from the resistance of the components. To this class belong those cases in which a very small quantity of an added element causes a very great increase in resistivity. Guertler has pointed out that this electrical difference between the compound and the mixed crystal lies in the fact that even a very small quantity of foreign element in the mixed crystal very greatly interferes with conductivity, while the pure *compound* of the elements is homogeneous and has a maximum conductivity, just as the pure element has.

The fact that the presence of certain impurities in very small amounts in metals such as copper and iron affects the properties to a very great extent, is well illustrated by the effect of arsenic, phosphorus, oxygen, etc., upon the electrical conductivity of copper. Addicks, Hofmann, Haen, and others, have published

curves of resistivity and composition from which it appears that even so small a quantity of arsenic as one-tenth of one percent reduces the conductivity of the copper by 30 percent. A similar result was obtained by adding aluminum. These marked effects ought to call for interesting details in the electron theory of metallic conduction, and they also point to the importance of continued improvement in copper refining, where the metal is to be used for electrical purposes. If traces of foreign matter are of such effect on the conductivity of copper, then it may well be possible that some of our present copper could be still further refined to advantage. It is fairly well-known that the present methods of refining yield copper whose conductivity is nearly two percent higher than the best obtained by Matthewson in 1861, when he gave us our value for pure copper.

If electric apparatus were made with two percent poorer copper than at present, the additional power loss per ton of copper used would be about $10 per year, at 1 cent per kw.-hr. (or $100, at the price most of us pay for current), at 50 percent load factor. As there are about one quarter million tons of copper used annually in the electrical industry, this two-percent difference in the copper resistance constitutes the considerable perpetually-acting conservation of power resources of 2½ million dollars a year. It seems highly improbable that this refinement of copper has reached the *"ne plus ultra"* stage, even from an economical standpoint. In the case of iron, where again high electrical conductivity is frequently of greatest importance, it has been shown that less than one percent of several other elements, such as carbon, silicon, arsenic, etc., reduce the conductivity to about half the value for pure iron. This knowledge is of double use. High resistance iron alloys, being cheap, are commonly used for their high resistance. All electric street cars carry a hundred pounds or more of such iron resistance. It is important to know the simplest and best way of producing the desired resistance combined with the other desired properties, such as mechanical strength and cheapness.

Who has not wondered at the changes in conductivity which are produced by annealing or softening hard metals? It seems to be a general rule that when a metal has been hardened by quenching from high temperature or by mechanical processes, such as

hammering or wire-drawing, the metal assumes a higher resistance by several percent, than it has in the soft or annealed condition. This fact must some day fit into the structure which the growing ionic theories promise us.

An exceedingly interesting case of conductivity is that which takes place in an arc. Here the electrodes usually determine the color, the luminosity or spectrum of the arc-stream, but it may be incorrect to assume that either of the electrode materials actually takes part in the conduction. The first opinions seem to have been that positively charged particles of the anode carried the current, but when experiments were tried with arcs between two metals in air, it was found that each of the metals appeared on the other electrode after an arc had passed. This, of course, might have been due to simple distillation as the electrodes become very hot. We were inclined to believe that the conduction of an arc was due to negative particles only, because at least in some and possibly in all arcs, the consumption of the negative electrode seemed alone the essential one. In such cases as the carbon arc, the positive electrode is apparently merely burned away by the action of the oxygen of the air on the hot carbon and distilled from the crater by the temperature locally reaching the subliming point. Positive electrodes of metal are in many cases practically non-consuming, while few, if any, arcs can be kept burning without waste of the negative electrode. So far as I know, a theory of the arc which postulated only a passage of negative electrons which caused some wasting away of the cathode, would cover the known phenomena of the arc. We are not even sure that the phenomena of an arc in a confined and partially evacuated space can be considered as similar to those in an arc at atmospheric pressure. In the former case, Sir Oliver Lodge recently advanced the hypothesis that the positive ions migrate from anode to cathode, where they are neutralized by negative electrons. Thus the conductivity involves a discharge at the anode of a negative charge from neutral atoms, which then, becoming positive, pass to the cathode as positive particles, to be there again neutralized. There are some good grounds for such an assumption, and while Townsend has stated the fact that positively charged surfaces do not in general give off positively charged particles nor give such charges to the

surrounding gas, still there are evidences in the canal rays that positively charged particles must be considered in vacuum tube conduction and probably also in arcs at atmospheric pressure. There can be little doubt that the positive ion, at least, in gaseous conduction, is soon going to become as firmly fixed in our vocabulary as it is in the case of electrolytic conduction.

It may seem useless to refer to such simple conductivities as those of aqueous solutions, but I am looking at various conductivities from the point of view of their similarities and differences without going into specific cases, which will be covered by other speakers. One of the first noteworthy points in our solution conduction is the fact that at ordinary temperatures it never reaches anything like the magnitude of the arc or metallic conduction. While we may by suitable selection of concentrations produce any desired low conductance value we cannot exceed about one ten-thousandth of that of metals. We find also in general a fairly uniform value for the effect of temperature on the electrolytic conductivity, but this is quite different in amount and sign from that of the metals. It usually lies between 5 and 6 times as great, for aqueous solutions at ordinary temperatures. In the case of aqueous solutions the evidence of the migration of ponderable material, both in negative and positive direction, is too convincing to be questioned, and the commonly occurring but not necessarily visible decomposition at the terminals of this type of conductor differentiates it from the metallic type.

May we not hope, too, that when the theories of conduction are well advanced we will have some conception of the process by which one piece of iron can be given a practically permanent power of attraction for another, particularly if the iron be mechanically a hard iron or steel? We know that this property may be temporarily imparted to soft iron by the passing of a current around it and that even when the iron is not included that the space around which the current is carried has an attraction for the element iron. These are old and simple phenomena, but they cannot be said to be completely understood. When this point is reached, the permanent and the temporary magnetic property should become explicable, with this, the explanation of the fact that our strongly magnetic metals are of nearly equal atomic weight will be in order, and thus the magnetic property of

oxygen, the effects of stress, of jarring, of compression, of temperature change, etc., in the case of magnetic materials will receive co-ordination. The pleasure gotten from contemplation of Nature's Laws is certainly a wholesome and warranted one.

[I will now call attention to the simple experiment previously referred to. I have suspended here six wires, each of 0.010 inch (0.25 mm.) diameter. They are copper, nickel, platinum (pure metals), German silver, ferro chromium, and nickel-chromium-iron (alloys). Each wire is connected to a single dry cell and has a little incandescent lamp in series with it. One contact on the wires is moveable, and I move these along the wires until all six of the lamps glow equally. The lengths of the six wires thus included in the separated circuits are now proportional to their respective conductivities and to the conductances of the materials in this case. You will note, for example, that a length of the ferro-chromium alloy of not over half an inch, has the same resistance as two feet or more of the copper, and that the ternary alloy in circuit is still shorter. All known metals and alloys come within the range thus illustrated. These wires are all at approximately the same temperature, as the current they are carrying is too low to appreciably heat them.

To show the effect of the temperature coefficient of resistance, I now surround each of the wires (without disturbing the contacts) by separate electric tube furnaces which heat each of the wires to 800° C. You note that as the temperature rises the lamp indicators on the pure metals gradually grow dim and finally go out, while only a slight and yet distinct and different diminution of the light takes place in the case of the three alloy-wire indicators. In general, then, the alloys have a low temperature coefficient, while the pure metals have nearly identical higher values of this coefficient.]

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE ELECTRON THEORY.

By M. W. Franklin

Conceptions of chemical affinity date from Albertus Magnus, who first suggested the term to denote the force with which different chemical substances cling together. Ideas of affinity have been varied since that time, and have been the subject of much speculation and controversy.

In 1718 Geoffroy compiled affinity tables in which he arranged acids and bases in the order of their acidity and basicity, respectively, as compared with some fundamental substance of the opposite kind.

In 1772 Beccaria first observed the relation between chemical and electrical action, when he succeeded in obtaining the phenomenon of reduction by the use of the electric spark.

Bergmann, in 1775, discussed the question of affinity, and stated that certain elementary substances were capable of uniting to form compounds whose chemical stability was a function of only their polar strengths, and while he totally ignored or even discredited the influence of mass, he, nevertheless, appreciably advanced the knowledge of chemical combination.

The contention of Berthollet, in 1801, that only the mass exerted an influence in chemical combinations, contained an element of truth and an element of error.

In 1793 Volta, investigating the phenomenon of "animal electricity" discovered by Galvani, concluded that the electricity was produced by chemical action resulting from the contact of two dissimilar metals, and in 1800 he invented the electrochemical battery. Its announcement was the starting point of a vast series of researches, whose results culminated in the theory of electrolytic dissociation.

The laws of multiple and constant combining proportions, enunciated by Proust in 1801-7, and finally crystallized into the

atomic theory by Dalton in 1808, formed the foundation on which the later works of Davy and Faraday were built.

During this period the general impression that there existed some connexity between heat, electricity and chemical action was fast gaining ground, and this view was strengthened by the successful decomposition of water in 1800 by Nicholson and Carlisle, by means of the Volta pile. This result was followed in 1803 by that of Henry, who electrolyzed nitric acid and sulphuric acid. Berzelius and Hissinger extended the process to the decomposition of the acids and bases of the neutral salts. Berzelius advanced the theory that each atom was itself charged with both positive and negative electricity, and that the ultimate electrical polarity of any atom was determined by that kind of electricity which was present in excess. The amount of this excess determined the "chemical strength" of the atom or aggregate. Ritter, shortly thereafter, produced electricity by chemical decomposition.

In 1807 Davy proposed a hypothesis according to which the ultimate particles of matter became electrified on contact and adhered because of the force resulting from the opposite charges thus brought into being.

One of the most important of the early observations was that of the deposit of gold on silver by means of the electric current, by Brugnatelli, in 1805. The fact that in the electrolytic decomposition of a metallic salt, or, in fact, of any other substance, one part appeared at the positive pole, and the other part at the negative pole, at once necessitated the assumption that the parts were oppositely charged. The observed phenomena admitted of no other explanation.

It was but natural that the observation of these interesting and apparently correlated phenomena should have stimulated speculation as to their exact theoretical foundations, and the literature of the period teems with more or less acceptable hypotheses. The theory of Grotthus for a long time carried much weight and has the distinction of having accounted for more of the observed facts than any of its contemporaries. It was obvious that the two components of the electrolyzed compound, appearing at they did simultaneously at two points remote from each other, could not have come from the same molecule unless the untenable assumption of practically infinite velocity

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in the electrolyte were made. Grotthus (1806-8) explained the fact on the assumption that the molecules arranged themselves in chains under the action of the electric force, and that the molecule nearest either electrode parted with its atom, which carried the charge of opposite polarity to that of the electrode. This would result in the momentary existence of a positive atom at the + electrode and a negative atom at the — electrode. The free charged atoms would then unite with the molecules of the electrolyte next adjacent and displace from it the atom of like electrification, and so by a series of repetitions the process would be transmitted from one end of the cell to the other.

In 1833 Faraday published the results of his researches on electrolytic decomposition. He had made a careful quantitative investigation of the phenomenon and deduced two fundamental laws which have been variously verified since his time. The starting assumption was that, as not any of the electricity was stored up in the circuit, the current resembled that of an incompressible fluid, and the current density must therefore be uniform in all parts of the circuit.

The current of a voltaic cell was passed into a branched circuit, each of whose limbs contained an electrolytic cell. The current from these two cells was united in a single conductor and passed through a third cell and thence back to the battery. This arrangement ensured that the current in the third electrolytic cell was equal to the sum of those in the other two. As *current* is the *time rate of flow* of electricity, it may be said that in a given time the same amount of electricity flowed through the third cell as flowed through the other two combined. Careful measurement showed that the amount of deposition was proportional to the time and to the current, or, in other words, to the quantity of electricity which passed through the electrolyte.

Faraday then placed several electrolytic cells in series, so that the same amount of electricity would have to pass through each, and he supplied them with different electrolytes. Measurement demonstrated that in each electrolyte the amount of deposition was proportional to the chemical equivalent weight of the substance deposited. From these facts it may be deduced that the elementary parts of any substance or group are associated with an amount of electrification proportional to their valency. Thus

in the electrolysis of water the volume of oxygen evolved is one-half the volume of the hydrogen liberated in the same time, and this and analogous facts in connection with Avogadro's hypothesis naturally lead to the supposition that each atom, or radical group, corresponds with a quantity of electrification commensurate with its valency.

Faraday's laws may be stated as follows:

(1) The mass of substance liberated from an electrolyte is proportional to the quantity of electricity which passes through the electrolyte.

(2) The mass is proportional to the chemical equivalent weight of the substance.

These laws may be expressed by the formula: $m = izt$: where m is the mass in grammes of the substance liberated in t seconds by a current of i amperes; z is the electrochemical equivalent of the substance, or the mass liberated by the passage of 1 coulomb.

Faraday apparently held the same views as did Grotthus, with respect to the theory, and he introduced the terms electrolyte, ion, anion, kation, anode and kathode, with their modern acceptations.

Faults in the theory of Grotthus were pointed out by Grove (1845), Williamson (1851) and Clausius (1857). Each of these substantially fore-shadowed the theory of electrolytic dissociation of Arrhenius, which appeared in 1887 and which is in many respects the most important single law of modern physical chemistry. Grove concluded from an examination of the reactions in the oxygen-hydrogen cell that the molecules exist, in the first place, in a decomposed condition and that the decomposition of water by the current is not a primary action.

Williamson proposed the hypothesis that in hydrochloric acid "each atom of hydrogen does not remain quietly attached all the time to the same atom of chlorine, but they are continually exchanging places with one another. If this is the case, then the two radicals must be present separately for a certain length of time, and this will be longer the farther apart the molecules are, or in other words, the more dilute the solution is."

In 1853 Hittorf examined the question of the unequal concen-

trations which existed in the electrolyte near the two electrodes, and discovered that the ions moved with different velocities.

St. Claire Deville (1866) studied the subject of dissociation and paved the way for the work of Kohlrausch.

An important advance was made by Kohlrausch in 1879 when he assumed that the current was the streaming of the ions in opposite directions, and that these ions, each possessing a definite charge, were the medium of the transfer of the electricity. The current was thus assumed to be an additive function of the number of ions passing a given plane in a unit of time, and of the charge on the ions.

Clausius arrived at the conclusion, that the assumption of the components of the molecule being attached to each other permanently was incorrect, from having observed that the electrolysis of silver nitrate could be effected at voltages far lower than those corresponding with the energy of formation of silver nitrate.

Arrhenius, from a consideration of the researches of van't Hoff on osmosis in salt solutions, promulgated the theory of electrolytic dissociation. This theory states that some of the atoms of the molecules of an electrolyte exist independently and each is capable of exerting its own influence in precisely the same manner as if it were an independent molecule of the electrolyte. The theory further postulates the existence of an electric charge associated with each of the ions, and concerns itself with the degree of dissociation as a function of the dilution and of the nature of the salt.

The conduction of electricity by solutions, as developed above, may be summarized as follows:

α. When an electrolyte is dissolved in a suitable solvent, some of the molecules dissociate, *i. e.*, break up into their component ions, which manifest opposite electrical properties.

β. The amount of this dissociation is proportional to some function of the dilution and to the nature of the salt.

γ. The charge associated with each ion is proportional to its valency.

δ. When an electric field is applied to the solution of the

electrolyte, the negative ions or anions migrate to the anode, and the positive ions, or kations, to the kathode.

ϵ. Chemically equivalent quantities of all substances are liberated by the same quantity of electricity.

Reasoning from the above facts, the atomic structure of electricity might have been deduced, and sufficient data from which to determine the magnitude of what is now generally accepted to be the ultimate electric element were in existence as the result of the researches of, for the most part, chemists.

The value of the electrochemical equivalent, *i. e.*, that quantity of electricity necessary to deposit one chemical equivalent weight of any substance, was roughly determined by Faraday, and the determination has been accurately made from time to time since. The value 9.65×10^3 electromagnetic units is the mean of those obtained by Smith, Mather and Lowry (1907), Kohlrausch (corrected 1908), and Janet, Laporte and de la Groce (1909-10).

Let $\rho = 9.0 \times 10^{-5}$ gm. be the weight of 1 c.c. hydrogen, at standard conditions (s.p.t.).

Let $N = 2.8 \times 10^{19}$ be the number of molecules per c.c. hydrogen (s.p.t.).

Let $Q = 9.65 \times 10^3$ electromagnetic units, (e. m. u.) be the electrochemical equivalent.

Then, since the hydrogen molecule is diatomic, the mass of the hydrogen atom is $m = \frac{\rho}{2N}$

The electricity required to deposit 1 gm. hydrogen is $q = \frac{Q}{1.008}$

hence the quantity associated with 1 hydrogen atom is

$$e = mq = \frac{\rho Q}{2N \times 1.008}.$$

The value of N has been determined by several methods, *viz.*:

Cloud formation and Stokes' law	2.78×10^{19}
Counting α particles	$2.78 \times$ "
Theory of radiation	2.76 "
Brownian movement	3.17 "
Mean value	2.8×10^{19}

Substituting the known values in the above equation we have:

$$e = \frac{9.0 \times 10^{-5} \times 9.65 \times 10^{3}}{2 \times 2.8 \times 10^{19} \times 1.008} = 1.54 \times 10^{-20} \text{ E. M. U.}$$

$$= 4.62 \times 10^{-10} \text{ E. S. U.}$$

No smaller electrical quantity than this has been observed associated with any chemical or physical phenomenon, but on the other hand exact multiples of it have been demonstrated in many chemical processes, as mentioned above.

While the preceding facts were laboriously being won, speculation on the ultimate nature of electricity occupied the thoughts of many of the most distinguished scientists of the various chronological periods through which the development passed.

In 1600 William Gilbert published his great work "De Magnete," and the circumstances may be said to have marked the emergence of electrical science. The knowledge of the time consisted solely in a few scraps of information on the behavior of various substances when rubbed, and Gilbert's work was an attempt to collate these into some semblance of a treatise.

Otto von Guericke produced the first electrical machine, which was a vast improvement on the sticks of glass and of sealing wax of his predecessors. It consisted of a sphere of sulphur mounted on an axle which could be rotated. When the hand was used as a rubber on the sulphur sphere the phenomena of frictional electricity could be produced on a scale which transcended that of anything which had been done previously.

Sir Isaac Newton produced a similar machine with glass substituted for the sulphur.

In 1709 Francis Hawksbee showed that metals, if suitably insulated, could be electrified as well as the non-metals, with which the phenomenon had always been associated until that time. He also pointed out that the electrification of a metallic body was confined to the surface only.

In 1720 Stephen Gray discovered that hair, silk, wool, paper, etc., could be electrified by friction, and in 1729 he discovered the difference between insulators and conductors when he tried to insulate a suspended conductor by means of various suspensions.

An observation of great importance in the development of

electrical theory was that of Dufay who, in 1733, perceived that there were two kinds of electricity, which exhibited opposite polarities. He observed that unlike kinds of electricity attracted each other and that like kinds repelled, and he formulated the first two-fluid theory of electricity. It was likewise known to Dufay that the force between two electrified bodies varies with the distance, though he did not arrive at the exact law.

Ellicott, about 1736, enunciated the view that "the particles of the electric fluid repel each other, while they attract those of all other bodies" and this seems to be the first recorded reference to the idea of a discrete particulate structure of the electric fluid.

The accidental discovery of the Leyden vial in 1745 greatly stimulated research along electrical lines. This apparatus, the identity of whose discoverer is the subject of some uncertainty, put at the disposal of physicists the means of observing electrical phenomena quantitatively, and incidentally it enabled them to work with vastly greater electrical charges than had previously been attainable.

In 1746 Le Monnier independently discovered the fact that the electrification of a charged body resides only on the surface, and he regarded this as confirming Ellicott's view that the particles of the electric fluid repel each other.

Sir William Watson (1715-1807), who performed important experiments on the conduction of electricity to a distance and who first suggested coating inside and out with tin-foil the Leyden jar, which up to that time had consisted simply of a bottle of water, has sometimes been credited with having forecast the one-fluid theory of electricity.

The one-fluid theory of electricity, developed by Benjamin Franklin, appeared in 1750, and it is, with the exception of some minor details and the lacking of some facts which have been discovered lately, substantially the accepted theory of electricity of the present day. Recognizing that the coatings of the Leyden jar were electrified equally and oppositely, Franklin believed that the state of electrification was due to the absence or to the presence of a single subtle fluid—the "electric fire." Positive or + electrification he regarded as the addition of electricity to the quantity which always existed normally on unelectrified or neutral bodies. This natural electrification was supposed to be just as

much as would exert an attractive force on matter sufficient to balance the repulsion which it would ordinarily exert on an equal quantity of free electricity in the immediate neighborhood. Negative or — electrification he supposed to be the subtraction from ordinary matter of some of the + electricity which is naturally associated with it.

Aepinus in 1759 published an elaboration of the one-fluid theory, in which he postulated some of the most vital attributes of the modern electron theory. The theory of Aepinus was founded on the assumptions:

α. The particles of electricity repel each other with a force which is an inverse function of the distance.

β. The particles of electricity attract the atoms of matter and are in turn attracted by them.

γ. Electricity exists in the pores of all matter, in which it moves about with ease in the case of conductors, and not at all in the case of insulators.

δ. Electrical phenomena are the result of the transfer of electricity from one body to another or of the repulsion or attraction of charges when there is no transference.

A modification of the two-fluid theory which contains some interesting and important features bearing on the modern theory, was advanced by Robert Symmer in 1759. The essential feature of Symmer's theory was that the two electricities are interdependent and that the neutral body possesses, at all times, equal quantities of both positive and negative electricities. The phenomenon of negative electrification, on this view, is simply the absence of some of the usual postive electricity, and positive electrification is the absence of some of the usual negative electricity.

The earliest mention of what is now a well-recognized phenomenon, *viz.*, the conductivity imparted to air by a charged body, was made by Beccaria in 1770.

Cavendish in 1773, from purely mathematical reasoning, determined that the charge is entirely on the surface of a conductor, and deduced the law of inverse squares for the attraction between electrified bodies.

In 1785 Coulomb proved the law of inverse squares by a series of remarkably precise measurements.

The next important step was the discovery of "animal electricity" by Galvani, already alluded to. The work of the physicists from this period on merges into that of the chemists insofar as theories of the nature of electricity are concerned.

Laplace, Volta and Lavoisier, toward the end of the 18th century, discovered that evaporating fluids produce electricity. They found that bodies caused to assume the gaseous state, in an insulated vessel, communicated a high potential to the latter, and at the same time it was noted that the electricity produced was always negative.

At the beginning of the 19th century the trend of electrical investigation was along the lines of the application of the mathematics to electrical problems. The subject of magnetism with its increasing number of recognzed relations to electricity claimed a substantial share of scientific attention. This period has been made memorable by the work of Biot, Poisson, Laplace, Oerstedt, Ampere, Faraday and Davy.

In 1821 Davy observed the deflection of the voltaic arc under the influence of the magnetic field, but no important comment on the probable cause of the phenomenon is to be found in his writings. This discovery and that of Walker, who in 1840, produced rotation of the vacuum tube discharge by a magnet, are of singular interest in view of the importance which similar phenomena have latterly assumed in connection with the electron theory.

Faraday, reasoning from his experiments on magnetic and electric induction, laid great stress on the importance of the phenomena in the medium surrounding electrified bodies, as compared with that of those in the bodies themselves. He found it impossible to comfortably accept the idea of action at a distance, and so he conceived a complex and ingenious system of lines and tubes of force in the dielectric medium, by means of which he was able to explain all of the observed electrical phenomena. Faraday did not so much discredit as ignore the existence of tangible electricity, but his attitude profoundly influenced opinion on electrical theory for upward of sixty years, and many of his

followers professedly did not believe that electricity was anything more than the manifestation of a state or condition.

Plücker was probably the first to have noticed the green fluorescence on the wall of the vacuum tube opposite the kathode. He regarded this as due to rays from the kathode which struck the glass and were reflected toward the kathode again. He also studied, in some detail, the action of the magnet upon the kathode rays, and discovered that this action differed from that exerted on the positive column.

About 1855 De la Rive studied the conduction of electricity in rarified gases and verified much of the work which had been done previously. He speculated somewhat on the Aurora Borealis and promulgated a new theory for its causation.

Hittorf in 1869 independently discovered the fluorescence which is caused when the kathode stream impinges on the wall of the vacuum tube. He anticipated Crookes in many experiments and observed the magnetic deflection of the kathode stream. He regarded the kathode rays as motion which was associated with something tangible which proceeded normally from the kathode. He also showed that if a body, either conducting or non-conducting, was interposed between the kathode and the tube wall, there resulted, in consequence, a shadow.

Faraday examined, at great length, the phenomena of discharges in gases and arrived at the opinion that the flow was convective and that the gas particles became charged spheres which carried the electricity.

In 1873 Maxwell used the expression "atom of electricity," which he regarded as a convenient imaginative figment to serve a certain purpose of elucidation. He was careful, however, to cautiously qualify his supposedly lax usage and stated that the conception would in all probability find no further justification when the true nature of electricity should have become known.

The first authentic statement of actual conduction of a normal gas was made by Herwig, who, in 1874, noticed that mercury vapor would sometimes apparently become conducting. His experiments were not accepted as authentic for the reason that at the time, gases were regarded as perfect insulators even under conditions of rarefaction. Boltzmann and Maxwell had shown experimentally that such gases as they had worked with including

air, steam, mercury vapor and sodium vapor were nonconductors even at very high temperatures. A résumé of the subject was published by F. Braun in 1875 in which the single exception to the nonconductivity of gases was stated to be the heated gas from a Bunsen flame, which, it was said, conducted very well. The whole subject was enshrouded by so many apparently inexplicable incongruities that no one of the many explanations hazarded, was generally accepted. At the time it was regarded as reasonably certain that the loss of electricity from insulated bodies, in contact with air, which had been observed by Reiss and Coulomb, was due to leakage along the supports alone.

One of the most remarkable forecasts of the present-day theory of electricity was that of Weber, who, in 1875, stated that electricity was composed of minute particles, smaller than the atoms of matter. His conception scarcely differs from the electron theory, with the exception that it regards the electric elements as composed of positive instead of negative electricity. In the light of what was then known of the subject, this exceptional circumstance hardly can be regarded as more than an inconvenient choice of signs, and it signifies that what was regarded as an excess of electricity, was in reality a commensurate lack, and *vice versa.*

In 1876 Varley studied electrical conduction in the Geissler hydrogen tube and found that a high initial voltage was required to start the discharge but that once started, it could be maintained with a much lower pressure. This seems to be the first mention of what has lately come to be understood as ionization by collision.

Goldstein, in 1876, repeated some of Hittorf's work with vacuum tubes and by making the obstruction in the path of the kathode rays, small, and placing it near the kathode, he proved by the sharpness of the shadow that the rays were straight, *i. e.*, normal to the surface of the electrode, which, in his experiments, was a small plane metallic disc. He regarded the kathode radiation as formed of ether waves.

Maxwell's description of the luminous discharge in air is interesting as very nearly approximating to the description which would follow from a recognition of the electron theory: "The electric glow is produced by the constant passage of electricity

through a small portion of air in which the tension is very high so as to charge the surrounding particles of air which are continuously being swept off by the electric wind which is an essential part of the phenomenon."

Sir William Crookes, in 1879, published the results of his investigations on the electric current in evacuated tubes. He had been able, through his ingenious modification and improvement of the existing types of air pumps, to secure much more perfect vacua than had his predecessors. He succeeded in obtaining a vacuum of approximately one millionth atmosphere, which figure has scarcely been exceeded to the present day, with pumps. Crookes reproduced all of the vacuum tube phenomena which had been obtained previously, and a great many new ones. He regarded the kathode radiation as being composed of matter in a new state, the "radiant" whose degree of subdivision exceeded that of the gases. The bombardment of this matter on a solid body, placed in front of the kathode, produced intense heat, and the already discovered shadow of Plücker and Hittorf. Besides this, Crookes constructed a light finely balanced windmill of mica and caused it to rotate under the impact of the kathode rays.

The theory of radiant matter was received with scarce more than contempt when it was announced, but there is little doubt of its legitimacy now.

In 1881 Dr. G. Johnstone Stoney pointed out that the indivisible charge, associated with the ion in electrolysis, constituted the natural unit of electricity and was one of nature's fundamental physical constants. He suggested the name electron for this unit electrical charge. Stoney actually calculated the magnitude of this charge from the then accepted value of the electrochemical equivalent and the number of atoms in 1 c.c. hydrogen as determined from the kinetic theory of gases.

In his Faraday lecture of 1881, Helmholtz said: "If we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid the conclusion that electricity both positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

This view though now generally current, and though supported by a wealth of all but incontrovertible evidence, by no means reflects the opinion prevalent at the time it was enunciated, as

will be evident on perusal of the following extract from the ninth edition of the Encyclopaedia Britannica (1881): "Following the caution of Coulomb and the example of Sir William Thomson, we shall avoid the term *electrical fluid* and substitute instead the more succinct and less misleading word *electricity*. We suppose that a body which exhibits electrical properties (as above defined) has associated with its mass a certain quantity of something which, *without attempting further definition,* we shall call *electricity*."

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE MODERN THEORY OF ELECTRIC CONDUCTION.

By D. F. Comstock.
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I am glad that Dr. Whitney has explained to you what I am going to say, because I feel a certain embarrassment in speaking about things which are not at all new. I hope you understand then that he has requested me to make no attempt to say anything new, but to review briefly the modern theory of the structure of matter, in so far as it bears on the theory of conduction, so that we may all visualize as clearly as possible, during the later papers, the intimate structure of a piece of matter as is at present known in fundamental physics. I shall, therefore, forego any further introduction and dive immediately into the heart of the subject.

From the standpoint of modern theory we have to consider three fundamental realities which go to make up the structure of a piece of matter as we see it—*the atoms, the electrons,* and the more or less mysterious entity which we know and call by the name *"energy."* This last, from the modern point of view, means *"electromagnetic energy;"* we leave out of consideration gravitation only. Gravitation, however, is a very weak force compared to the other forces, although strong, of course, when you have the whole earth as one of the attracting masses.

To summarize briefly the state of belief with regard to these three entities: I can say, first, that we now know about 100 different kinds of atoms (I say 100 because of the new radioactive elements). The approximate diameter of an atom is one-hundred millionth of a centimeter. In weight, the different atomic species vary from hydrogen 1 to uranium 240 approximately, and in volume, according to the best estimates, in about the ratio of the square roots of these numbers; that is the heaviest atom has about 240 times the weight of the lightest, and has about

16 times the volume of the smallest. This makes the radius of the heaviest about two and one-half times that of the lightest.

Of course, from the modern point of view the atom is by no means the simple object which it was thought to be years ago. Professor Rowland wrote that, compared with an atom, a grand piano is a very simple affair, and I think that modern research has certainly borne this out.

The electron was discovered by J. J. Thomson in 1896. From the modern point of view it is the ultimate unit of electric charge, and must be considered as very much smaller than the atom. It is very difficult to see how it can possibly be much smaller or much larger than 10^{-13} centimeter, so that it has a diameter only one-hundred thousandth that of the atom. Let us try to visualize clearly what this means. If you represent an electron by a pin head, an atom will have to be somewhere near the size of an office building.

It is important to realize the enormous difference in size between the atoms and electrons, if the mutual relations of the two are to be understood. Electrons, so far as we know, are only of the negative kind, no positive electrons being yet known.

The other fundamental reality, *electromagnetic energy,* is in a certain sense very much more mysterious, but it has a power of impressing one with its reality which, it seems to me, is becoming greater and greater. Radiant energy leaves the sun eight minutes before it reaches the earth, and if you imagine a flash of sunlight leaving the sun it certainly has, so far as we know, no effect whatever on the earth until these eight minutes are up. It has no forerunner, and on the other hand it leaves no trail behind. *It seems to be a definite isolated reality which is localized in space during these eight minutes.* We know that it is conservative, that is, that it cannot be created and destroyed. Again, we know that radiant energy exerts a force on any surface which absorbs it or reflects it, so that radiant energy has *momentum.* It is, therefore, very much indeed like matter in its action. It comes from a great distance with a high speed, strikes a surface, bounds back or is absorbed by the surface, and exerts a thrust upon it. Radiant energy can also be definitely localized, in the ordinary sense of the word, that is, it is at a certain place at any given instant. So that radiant energy, although perhaps

very mysterious, in that it is not just like matter, certainly resembles matter in a good many ways. From the classical point of view, of course, we are to consider it as wave motion in the ether, the total amount of energy in the wave motion being a constant during the eight minutes occupied in the passage.

There is great reason for believing that when electromagnetic energy is "bound," that is when it is the energy of a charged body, it is localized in the space surrounding the body and not "on" it. Hence even here it is energy in space and thus similar to radiant energy. There seems to be definite reason for believing the very widely accepted modern point of view that energy has mass, and it is even probable that it has weight. Thus, a charged body has a greater mass than an uncharged body, so that although the energy is "bound" and is not propagated in all directions, even then it imitates matter again in this way.

These three entities are the only clearly defined ones that we have at our disposal at present for building up our model of the physical world, that is, for making a model which we can use in our investigations and in co-ordinating other facts.

We are, of course, neglecting gravitation. As I said, gravitation is of a smaller order. The gravitational attraction between two electrons can be calculated, since their mass is known and it appears that their electrostatic repulsion is 10^{42} times as great. The only reason that the weight of objects is so great is that here the earth is the other factor in the gravitation force-product, and being so enormous it raises this minute force into one which is of such extreme importance in the world. Consequently, in a first approximation we can leave out gravitation, as it is extremely unimportant in this connection.

Any modern theory, conduction or otherwise, if it is to be in line with modern views on matter must express itself in terms of *atoms, electrons* and *energy*. If it does not do so it is a distinct departure and as such must stand entirely on its own feet; it can get little help from the main body of present day thought and knowledge along these lines.

We are forced to believe that the atoms of solids, liquids and gases are in constant vibration. In the case of gases the atoms or molecules (the molecules being, of course, the small groups of atoms) are so far apart compared to their size, that they move in

straight lines, like billiard balls, until they hit other molecules.

Molecules must be considered as perfectly elastic. This is not an artificial assumption because the lack of elasticity in an ordinary substance, a piece of metal let us say, means that when it is rubbed the energy goes into the molecular or atomic energy of vibration, so that frictional forces correspond to the transformation of ordinary mechanical into molecular energy. According to modern theory, therefore, a body is inelastic *because* it is composed of atoms and molecules which are set into motion and thus absorb energy.

The space between the atoms, in an ordinary piece of matter, or in line with what Prof. T. W. Richards would have us say, the compressible atmosphere that must exist around the atoms, must be of the order of magnitude of the atomic radius itself, and as a body shrinks owing to the removal of the energy of vibration of the atoms, these holes, if you adopt the 'interstices' view, or this 'compressible region,' diminishes in volume until you have at the absolute zero, if you could reach it, no motion and no space between, or a very small compressible region.

As I said, the positive electricity does not appear in the form of electrons; it is always associated, apparently, with the atoms. Consequently, the charging of an atom negatively means that you in some way succeed in getting another electron on it. All atoms appear to have some attraction for electrons.

Charging an atom positively means that one of the electrons which it contains is taken out of it, leaving it, therefore, under the domination of the mysterious positive electricity which always remains in the atom. An uncharged atom must be considered, therefore, as an aggregate of a large amount of positive electricity combined with a number of electrons which, in the aggregate, completely neutralize the positive electricity. Charging an atom positively means removing an electron. Charging an atom negatively means putting an extra electron on the balanced atom.

I think we can say with considerable probability of being right that a great many of the properties of the atoms can be interpreted in terms of their attraction for electrons, the atoms of the so-called "positive" elements having a relatively small attraction for electrons and those of the "negative" elements having a relatively greater attraction for electrons. Consequently, if you

imagine a positive and a negative element mixed in such a way, and with sufficient vibration (*i. e.*, temperature), so that there can be an easy interchange of electrons between them, it will not be very long before you will have each negative atom in possession of an electron or two, stolen, as it were, from a positive atom. When this happens there will be a tendency for molecules to form, each containing a positive and negative atom, and it seems possible that chemical affinity may be explained along this line.

With regard to charging a body or passing electric current through metal: If you charge a piece of metal negatively it means, on this view, putting some negative electrons on it. The relative amount that you can add, that is, the number of electrons added compared with the electrons already on it, is very small. It takes but a very simple calculation to show that when you have increased the number of electrons on a piece of metal by one part in a thousand million, you have raised it to a negative potential of more than a million volts. The point which this brings out clearly is that you must not expect, in any electric operation, to find that you are exhausting the possible charge which the body contains, because it is almost inconceivably enormous.

We can say in a general way that all uncharged bodies must be thought of as containing practically an infinite amount of positive and negative electricity in exactly equal quantities.

Electrification by induction is to be considered merely as a *separation*. The electrons in the body of a metal, which consists of positive atoms, can move freely probably because of the smaller attraction of such atoms for electrons. When a charged body is brought near the piece of metal the electrons tend to move toward one end. In so doing they cause the end they go to to be negatively charged, and the end they leave, positively charged. As I said before, the amount of negative electricity which is on the negative end *above* what was there when the body was neutral is extraordinarily small. If this were not true, and you went on increasing this charge you would get to a place where the separation would not be in proportion to the force, of which there is not the slightest evidence.

Now, in the case of the insulator, if you put a positive charge near, there is precisely the same tendency for electrons to move

as in a metal. However, in the insulator, presumably because insulators are composed largely of negative atoms, the electrons cannot get out of the atom, and what they do is not to move large distances at all, but simply to shift their position slightly within the atom. Since on the average there are about 10^{22} electrons per cubic centimeter, even a shift of position of a fraction of an atomic diameter is enough to cause marked apparent displacement and the appearance of the pseudo-charge on the surface of the dielectric.

If you put a dielectric in the field, therefore, you get exactly the same *kind* of effect as when you put a conductor there and induce a charge, but the separation does not go on until the potential is the same throughout, but only to a degree depending on the flexibility of the electronic bond, which corresponds to the dielectric constant of the insulator.

Now, if an electric force is put on a conductor, the electrons will tend to move along in the same general way that ions move in an electrolyte, with this important difference, that in the electrolyte both ions move, whereas in this case, the thing being a solid, the positively charged atoms remain in the same position and the electrons, being so very much smaller, move between them or through them. Consequently what is moving in the wire is probably the electrons. To be sure, it happens to be in the opposite direction to what we call, for historical reasons, the direction of the current, but that is a trifling matter.

Knowing the charge of an electron, which is now known with considerable accuracy, and the number per cubic centimeter of the metal, it is possible to get an idea of the speed of the electrons through the metal for any given current density. I will only attempt to give this in round numbers. It is not the enormous speed called "the speed of electricity." It is of the same order of magnitude as that of the ions in an electrolyte—a few centimeters per second even in the case of large current densities.

What travels with the enormous speed so often mentioned is not the electrons, *but the impulse to move*. When we pull on a long rope or wire the other end moves, but only after a very short interval, showing that there is a force which is propagated.

This impulse is propagated with great velocity, whereas at no time may the rope itself be moving faster than, say, a foot a

second. In the same way the impulse of the electronic motion travels quickly, but the actual motion of the electrons must be very slow.

This is important to recognize, because I have found many people who have difficulty in visualizing this modern view of the electron and who keep in their minds a picture of the electrons shooting through the heart of the metal with the velocity of light. It is a very slow motion, and it is the impulse that propagates.

We can say in general, then, that the conductivity of any substance, that is, the current density for unit voltage, must depend on three things: *The number of electrons or ions, the charge they have on them* (which can only go up in steps of one, two, three, etc., and cannot be two and a half), and *the frictional resistance* which they meet in moving along, that is, the retarding effect of the molecular complex through which they move.

Hence, whether the ions or electrons are in gases or in liquids or in solids, we have these three factors which must be thought of if we try to visualize the thing and form a definite view of the way the electric current flows.

Hence we do not have the propagation of wave motion or the flow of ether or any other such thing through the wire, if modern ideas are correct. We do not have anything more mysterious than the bodily movement of electric charges.

Strictly speaking, the conception of the "conduction current" has disappeared. All currents are "convection currents," with the exception of the totally different thing which is called the "displacement current" (merely a change in the number of lines of electric force in space). The currents we have to deal with in electric currents are convection currents and not conduction currents, although conduction is a more convenient word.

If I have succeeded in outlining the model of a piece of matter, with its atoms and electrons and electromagnetic energy, which modern atomic theory contemplates, and if I have succeeded in making it vivid enough to lay the foundation for the more profitable papers which are to follow, I shall feel more than satisfied.

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE CONDUCTIVITY OF SOLIDS.

By E. WEINTRAUB.
(Director Research Laboratory General Electric Co., Lynn, Mass)

President Whitney has asked me to present the subject of the conductivity of solids in a "practical and simple manner," as he expressed it. In accordance with this I intend to give you a summary of the facts as far as I know them, leaving all hypothetical assumptions aside. I believe that others will give you an exposition of the now prevalent electronic theory as applied to conduction in solids. Admittedly, this theory is as yet in a crude state and not capable of explaining the complex phenomena exhibited by solids.

The laws governing electric conduction in solids and its relation to other physical properties are known to only a limited extent. Until we know more about the internal structure of solids, from which all their physical properties derive, it is, I believe, no more possible to give a satisfactory theory of electric conduction than it is to give a theory of hardness, density, etc.

In the first part of this lecture I will treat the conductivity of solids *per se,* and in the second the relation of electrical conductivity to other physical properties. In each part it will be convenient to consider under separate headings, (1) THE ELEMENTS, (2) THE SOLID SOLUTIONS, and (3) THE CHEMICAL COMPOUNDS. This subdivision is made merely for practical reasons.

A classification into "good" and "poor" conductors, according to the magnitude of conductivity, will be shown to conform better to natural lines.

PART I.

ELECTRICAL CONDUCTIVITY OF SOLIDS.

A. Values for Different Substances and Temperature Coefficient.

(1) ELEMENTS.

The values of the conductivities of elements at 0° C. are given in Table I, in reciprocal ohms $\times 10^{-4}$. With change of reference

temperature the values, of course, would change, but the position of the different elements in the table would not be materially altered provided extremely low or extremely high temperatures are excluded. The elements are arranged in the order of diminishing conductivity The first two columns contain the metals—the "good" conductors. Their conductivities vary between relatively narrow limits, silver with 67 being the best conductor and bismuth with 0.9 being the worst. The third column contains the "poor" conductors known at present, with only two representatives among the elements: silicon and boron. The fourth column contains the insulators and other than the gaseous elements, which are not considered here, and includes only three elements: phosphorus, sulphur and diamond.[1]

Between the "good" and "poor" conductors stands the element carbon, to which a separate column is given in the table. As "metallized" carbon, this element has a conductivity approaching that of bismuth; as "amorphous" carbon it has a high resistance approaching that of silicon. Finally, as diamond, it takes its place among insulators.

This division into "good" and "poor" conductors is warranted by the fact that the conductivities of the two classes are of different magnitudes. The poorest metal conductor, bismuth, has a conductivity of 0.9 while silicon has a conductivity of approximately 1.8×10^{-4}, or only about one five-thousandth of that of bismuth. This division will find further justification later on when amplified by the addition of a number of solid solutions and compounds, the class of "poor" conductors will then have grown to a respectable size, and it will then be evident that the behavior of the two classes is opposite to each other in almost every imaginable respect.

The values given in the table are not very accurate. The conductivity of elements is very much affected by the presence of small amounts of impurities. On this account the true conductivity values are probably higher than those given in the table. The conductivity values depend also on the physical state of the metal, whether hard or annealed, in fact on the whole history of any particular sample. Thus in silver the difference in conduc-

[1] So-called insulators must be classified with the "poor" conductors, the change of temperature often transferring a substance from one class into the other.

tivity between the hard and soft state may amount to 6-10 percent, in copper to 2-3 percent, in tungsten and molybdenum to even as much as 15-20 percent. The effect is seen to be a large one and is chiefly due, I believe, to differences in the coarse internal structure, which can be revealed to a certain extent by the microscope. A metal is an aggregate of crystalline grains and the size of those grains differs in the hard and soft state. In an

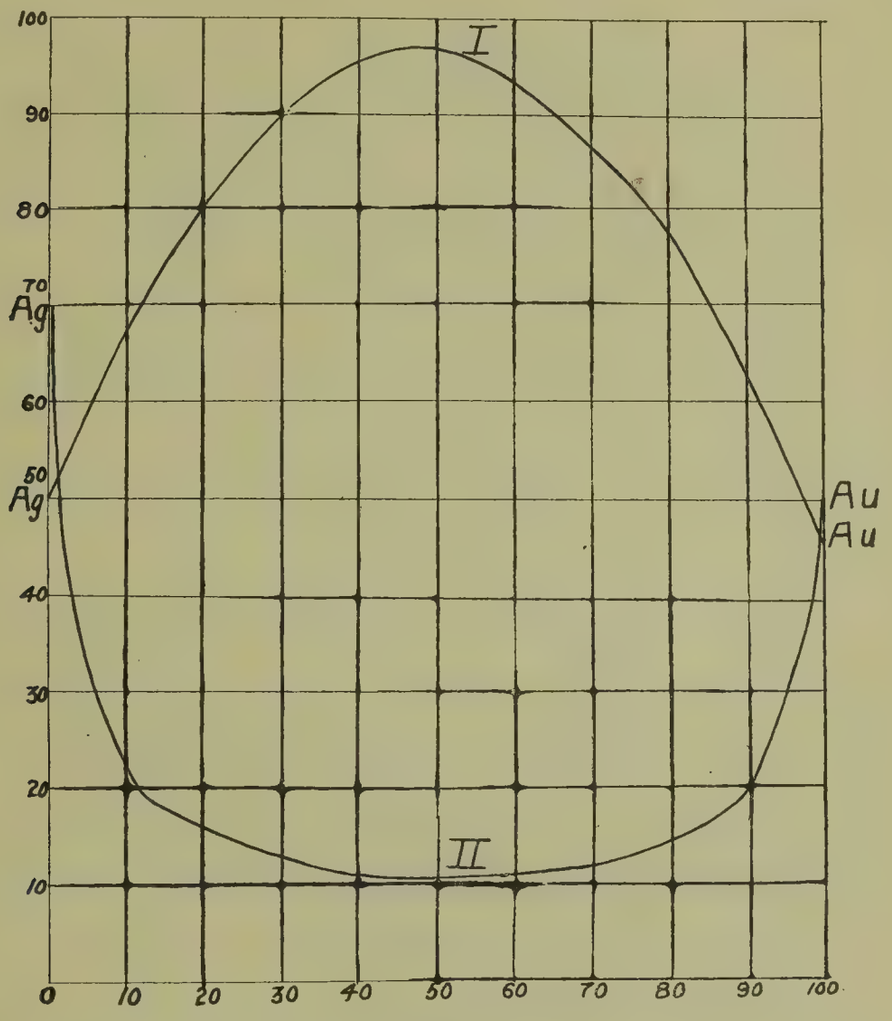

FIG. 1.

annealed metal the crystals are larger; in a metal which has been mechanically worked the crystals are broken up and a part of the metal is even reduced to an "amorphous" structure (according to Beilby). As a metal in an annealed state has a higher conductivity than in its hard state, we can explain the difference by assuming that in passing from crystal to crystal an additional "contact" resistance is added. As the crystals grow in size the number of boundary surfaces, and, therefore, of "contact"

resistances diminishes and the conductivity increases. In the present state of our knowledge of molecular physics it is impossible to further elaborate this point of view or to calculate the "limiting" conductivity of the metals.

The value for silicon is very uncertain, as most measurements were made with impure silicon and the results of no two observers agree. The difference in the size of crystals of cast rods due to different degrees of chilling is another cause of discrepancy.

TABLE I.

Conductivity of Elements at 0° C. *(Rec. ohm, cm.* $\times$ 10^{-4}.*)*

	Ag	67	Pd	10			
	Cu	64	Os	10			
	Au	46	Pt	9.9			
	Al	37	Sn	9.8		Si	Phos.
	Mg	24	Rb	7.8		1.8 $\times$ 10^{-4}	
	Na	21.1	Ta	6.8	C		Sul.
W, Mo,	Ir	20	Tl	5.6			
	Rh	18	Nb	5.4	Met. | Graph. | Amor.		
	Zn	17.5	Cs	5.2	0.2 | 0.0314 | 0.003		Diamond
	K	15	Pb	5.1			
	Cd	14.6	Hg	4.5			
	Ni	14.4	Sr	4.0		B	Gaseous
	Li	11.9	As	2.86		0.6 $\times$ 10^{-10}	Elements
	In	11.9	Sb	2.6			
	Fe	11.5	Ga	1.9			
	Co	11.	Bi	0.9			

The value for boron is only approximate, as my measurements were made on an irregular piece. I hope soon to find time to carry out the measurements on regular pieces, which I have since learned to produce.

The figures given for carbon have only an illustrative value, as carbon cannot be fused and the porosity differs greatly from sample to sample.

(2) SOLID SOLUTIONS OF ELEMENTS IN ONE ANOTHER.

Solid solutions which embrace only "good" conductors have a conductivity considerably lower than that of the constituents; the curve connecting conductivity with composition has the form of Curve II (Fig. 1), which refers to solid solutions of silver and gold. The conductivity, as seen from the curve, drops very

fast on addition of even small amounts of one constituent to the other. When the solid solution is dilute in one constituent the increase of resistivity is nearly proportional to the atomic concentration of the solute. Thus, according to Benedict, the resistivity of iron is increased by 5.9×10^{-6} for each atomic percent of the dissolved second constituent.

Solid solutions composed of a "good" conductor and a "poor" conductor show a different behavior. Each one of the con-

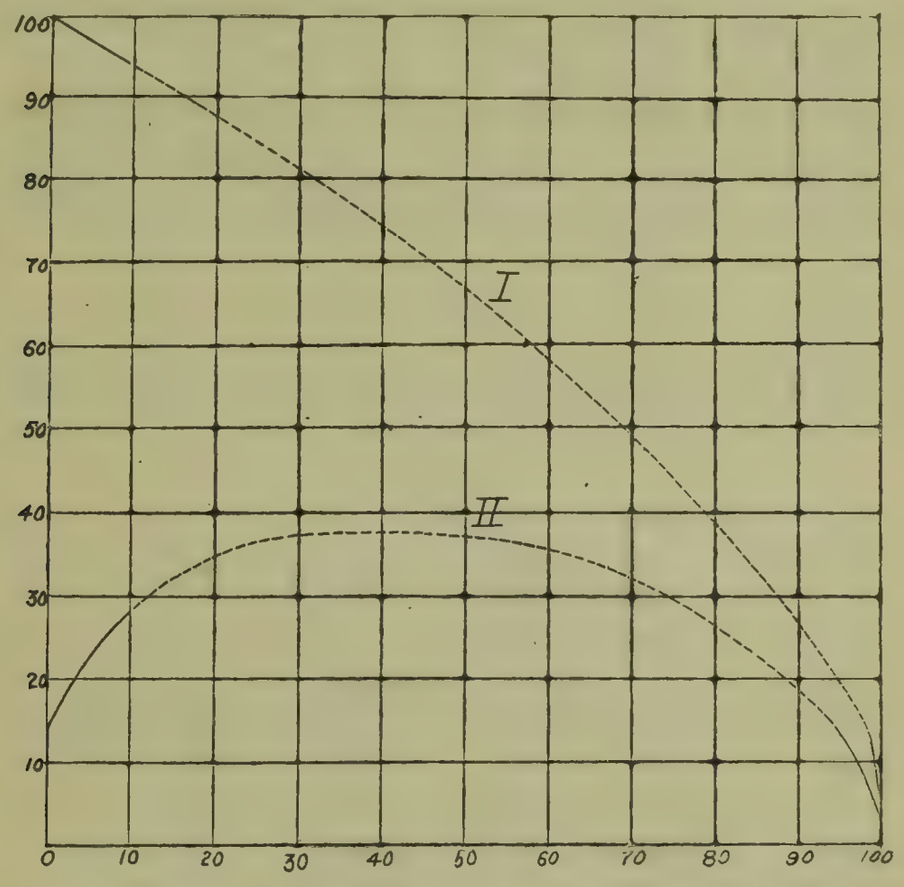

FIG. 2.

stituents tends to impress upon the solution its own characteristics. Thus the conductivity of boron is greatly increased when a small amount of a metal is dissolved in it; addition of a small amount of boron to a metal will, however, diminish the conductivity of the latter. The curve connecting conductivity with composition has, therefore, at its ends, the shape shown in Curve I, Fig. 2. The complete course of the curve is not known.

The same is true, as far as my knowledge goes, of carbon and silicon.

Solid solutions composed of two "poor" conductors show a

higher conductivity than that of the solvent. Thus an addition of a small amount of carbon to boron or of a small amount of boron to carbon increases the conductivity of the solvent in either case. The conductivity-composition curve has, therefore, at its ends the shape of Curve II (Fig. 2).

(3) CHEMICAL COMPOUNDS.

Coming now to chemical compounds corresponding to definite formulæ, we have first to consider the intermetallic compounds such as Mg_2Pb, Au_3Zn_5, $NaHg_2$, etc., etc.

The data on these are not numerous, and all that can be said is that their conductivity is usually lower than that of pure metals. This could be expected from analogy with the solid solutions.

TABLE II.

Conductivity of Solid Compounds at 0° C. (Rec. ohm, cm.).

Comp.	X_0	
CuS	0.85×10^4	Pos. Temp. Coef. of Res.
PbO_2	0.43×10^4	
CdO	0.083×10^4	
PbS	0.042×10^4	

Comp.	X_0	Comp.	X_0
FeS $\perp$ c axis	0.22×10^4	Fe_2O_3 $\perp$ axis	2.3
FeS $\parallel$ c axis	0.18×10^4	Fe_2O_3 $\parallel$ axis	1.14
Fe_3O_4	0.0116×10^4	Cu_2O	0.025
FeS_2 (Pyrite)	0.0042×10^4	Quartz	10^{-14}
FeS_2 (Marcasite)	0.060	Rock salt	10^{-17}

True compounds of "good" and "poor" conductors and of two "poor" conductors may or may not conduct. Our knowledge of the phenomena exhibited by these compounds is limited and it is at present impossible to predict from the composition to which class a compound of this nature belongs.

Thus iron carbide, Fe_3C, is a conductor; aluminium carbide and calcium carbide are, however, apparently nonconductors. While solid solutions of aluminium and boron all conduct, a crystalline compound exists which is transparent and is a nonconductor. Again solid solutions of silicon and carbon are con-

ductors, but carborundum, the crystallized compound, is a non-conductor.

Among sulfides, oxides and nitrides a number of conducting substances are found. Table II gives the conductivity values at 0° for a number of these compounds.

The conduction in most of these substances, such as galena, pyrites, hematite, etc., is wholly "metallic." In magnesium oxide, quartz and a number of similar compounds a certain small portion of the conduction seems to be electrolytic. The conductivity of most of these compounds is such as to class them among the "poor" conductors, and it is characteristic, as in the case of the "poor" conductors among elements, that mixtures or solid solutions of sulfides or oxides conduct better than each one separately.

Some nitrides are excellent conductors, for instance, titanium nitride; some others, such as aluminium nitride are non-conductors. A further discussion of the conductivity of these solid compounds will be found later on, when the influence of temperature on conductivity in general is considered.

B. Influence of Temperature on Conductivity.

(1) ELEMENTS.

In considering the influence of temperature on the conductivity of solids it will again be necessary to distinguish between "good" and "poor" conductors.

In "good" conductors the conductivity diminishes, or the resistance increases, as the temperature increases. The element mercury is perhaps the most suitable to illustrate this. We are fortunately in a position, due to the work of Kammerlingh Onnes, to state definitely that the resistance of mercury not only steadily diminishes as the temperature decreases but also that it becomes *nil* when the temperature approaches the absolute zero. Starting with absolute zero the resistance of mercury increases according to a parabolic formula up to near its melting point. During the change from solid to liquid, the resistance increases in the ratio of 4:1. On further raising the temperature the resistance of the liquid mercury continues to increase up to its boiling point. To complete the curve it would be necessary to know the resistance of mercury up to its critical tem-

perature. Strutt carried out experiments to this effect and, while he did not succeed in reaching the critical temperature, he has shown that the resistance of mercury continues to rise. Table III gives data taken from Dewar and Fleming on the resistance of mercury at different temperatures.

TABLE III.

Conductivity of Mercury at Different Temperatures.

C°	Cond. x10^{-4}	C°	Cond. x10^{-4}
350	0.7378	0	1.06285
300	0.7831	— 36.1	1.24410
250	0.8290	— 37.0	1.44
225	0.8577	— 38.1	2.205
200	0.8798	— 39.2	2.74
150	0.9226	— 40.7	3.46
100	0.9679	— 50.3	4.70
50	1.0148	—102.9	6.65
25	1.0386	—147.5	9.46
20	1.0444	—183.5	14.35
10	1.0535		

As I said above, the relation between resistance and temperature is given by a parabolic formula

$$R_t = R_0 (1 + \alpha t + \beta t^2)$$

in which β is a rather small coefficient. If β is neglected, and the temperature coefficient of resistance defined as $\frac{1}{R_0} \frac{Rd}{dt}$, we can say that the temperature coefficient of resistance of mercury is a constant quantity and for solid mercury at a sufficient distance from the melting point, is equal to about 0.004. The value for liquid mercury is approximately 0.001.

The behavior of other good conductors, such as copper, silver, aluminium, is similar to that of mercury. In all probability their resistance becomes *nil* at absolute zero. The curve connecting the resistance with temperature is parabolic and in those cases where measurements have been made up to the melting point a considerable change in resistance takes place at that point. Table IV gives this change for different elements.

Table IV.

Change of Specific Conductivity at Melting Point.

Metal	$\frac{X_{Solid}}{X_{Liq.}}$	Metal	$\frac{X_{Solid}}{X_{Liq.}}$
Li	2.51	Tl	2.0
Na	1.34	Sn	2.2
K	1.39	Pb	1.95
Zn	2.0	Sb	0.70
Cd	1.96	Bi	0.46
Hg	4.1		

The temperature coefficient of resistance can, within sufficiently narrow temperature limits, be considered as constant.

Table V.

Specific Resistance at Different Temperatures According to Niccolai.

Temp.	Pt.	Cu.
400°	25985	4093
350	24254	3797
300	22490	3512
250	20648	3207
200	18885	2888
150	17032	2565
100	15100	2249
50	13146	1921
9	11193	1577
— 50	9248	1251
—100	7212	904
—150	5200	558
—189	3580	302

Table V gives the conductivity of copper and platinum (in absolute electromagnetic units) according to Niccolai. Table VI gives the mean value of the temperature coefficient of resistance between 0° and 100° for a number of metals.

Table VI.

Mean Temp. Coeff. Between 0° and 100° C.

Sn	0.0044	Pb	0.0041
Al	0.0042	Zn	0.0041
Mg	0.0038	Cd	0.0042

Table VII, taken from the work of Somerville, shows the temperature coefficients of resistance for a number of metals at different temperatures.

It will be seen that the temperature coefficients of different metals are not far apart, and that the average value is not very far from that of the coefficient of expansion of gases. (0.00367) (Law of Clausius).

TABLE VII.

Temperature Coefficients of Different Elements.

Temp.	Au	Ag	Fe	Wo	Ni	Al	Mg	Cu
25	0.0025	0.0030	0.0052	0.0046	0.0043	0.0034	0.0054	0.0036
250	0.0030	0.0039	0.0100	0.0056	0.0078	0.0043	0.0042	0.0040
500	0.0036	0.0045	0.0155	0.0057	0.0029	0.0050	0.0036	0.0043
625	.....	.....	.....	.....	.....	0.0120	0.0250	0.0044
750	0.0039	0.0048	0.0250	0.0057	0.0027	.....	.....	.....
900	0.0049	.....	0.0050	0.0089	0.0037	.....	.....	.....

A somewhat exceptional position is occupied by the magnetic metals, iron and nickel, and also by tungsten. The temperature coefficient of resistance of iron is higher than that of most other metals and increases very rapidly with the temperature up to the so-called point of recalescence, about 750° C. After that temperature is passed the coefficient of resistance resumes a more nearly normal value. The same is true of nickel which, up to the temperature where it loses its magnetism, has a large and increasing temperature coefficient, which assumes more nearly normal values after that point is passed. (See Fig. 3).

With tungsten the temperature coefficient of resistance is higher than with most metals and constantly increases with the temperature, no critical region being observable.

From the known data it would seem as if the coefficient of resistance assumed abnormal values every time the molecular complexity of the material changes. Thus near the melting point of the metal the coefficient usually has abnormal values, causing the rapid change of resistance passing from solid to liquid. It also has abnormal values in magnetic elements near the point where the magnetic properties disappear, that is, the molecular complexity changes.

So much about "good" conductors. An entirely different behavior is shown by the "poor" conductors such as silicon and boron, etc. Their resistance instead of increasing with the temperature rapidly decreases; at absolute zero their resistance is probably infinite. (It is probably infinite for practical purposes before the absolute zero is reached). Their temperature coefficient is accordingly negative.

The resistance-temperature curve of silicon was determined by Koenigsberger and while some doubt may be entertained as to the existence of the different modifications he assumes, the

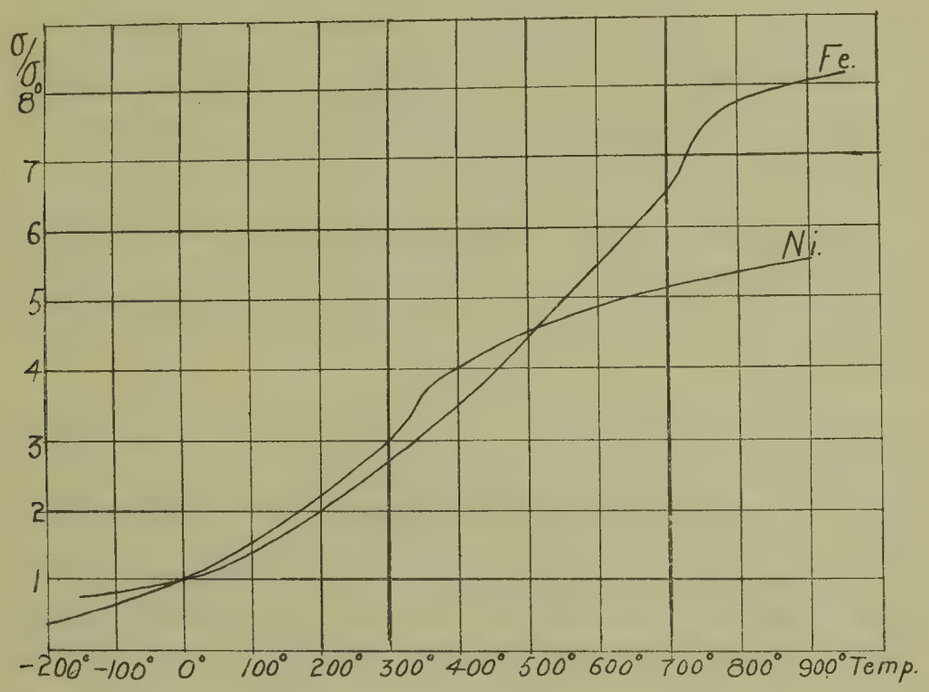

FIG. 3.

general downward trend of the curve is beyond doubt. With boron the measurements were made on a specimen of chemically pure element. The resistance drops with extraordinary rapidity.[2]

Not only is the sign of the temperature coefficient different from that of "good" conductors, but also the law of variation. The temperature-resistance curve is of an *exponential* nature instead of parabolic.

Carbon again forms the bridge between the poor and good conductors. As "metallized" carbon it has a positive temperature coefficient of resistance, which increases in the ratio of 2:1 between ordinary temperature and white heat; in its form as

[2] See Transactions of Am. Electrochem. Soc., **16**, 180 (1909).

natural graphite and amorphous carbon, its temperature co-efficient is negative. Graphite, compacted by a binding material which itself graphitizes on heating, has, according to Arsem, a negative temperature coefficient at low temperatures and a positive coefficient at higher temperatures, the temperature of minimum resistance getting lower as the porosity diminishes. Arsem believes that non-porous sintered graphite would have a positive temperature coefficient of resistance down to the lowest temperatures.

It was supposed, and the statement is found even now, that the sign of the temperature coefficient forms a characteristic distinction between metallic and electrolytic conduction, that metallic conduction is characterized by a positive coefficient of resistance and the electrolytic by a negative coefficient. In the light of what is said above this is obviously fallacious.

The discovery that chemically pure boron, in a fused homogeneous condition possesses at ordinary temperature perhaps the largest negative coefficient of all substances, puts to rest any such assumption.

The sign of the temperature coefficient is rather determined by the *magnitude* of the resistance, and although no sharp separation exists, in general, "poor" conductors (conductivity much less than 0.03×10^4) have a negative temperature coefficient of resistance; "good" conductors (conductivity much above 0.2×10^4) have a positive coefficient; in the region between, both positive and negative coefficients can be found. From this point of view, electrolytic conductors have a negative temperature coefficient because they are "poor" conductors.

Attempts were made recently (by Koenigsberger and others) to express the conductivity of both classes of conductors as a function of the temperature by means of one formula. This formula is a combination of the parabolic and exponential expressions. It leads to the conclusion that for every material there is a temperature of minimum resistance at which the temperature coefficient changes its sign.

The facts do not seem to favor this assumption. The work of Dewar and Fleming left it possible that in metals such a temperature could be found near the absolute zero. The work of Kammerlingh Onnes has, however, disposed of this possibility.

The author of the formula claims to have found in titanium a metal possessing a minimum resistance at the temperature of 150°. To any one who has worked with titanium it is well known how difficult it is to prepare this metal in pure state free from titanium nitride and titanium suboxide, materials which are relatively good conductors and have a negative temperature coefficient of resistance. A mixture of these materials with titanium would exhibit the behavior found by the author. It is true that in the case of compacted graphite a temperature of minimum resistance exists, but this is obviously due to the superposition of the positive temperature coefficient of the graphite material and of the negative temperature coefficient which is usually characteristic of contact resistance.

In "poor" conductors the minimum resistance could only occur at very high temperatures. I have made measurements in the case of boron up to the melting point, and in the case of silicon even a little beyond that, but found the resistance constantly diminishing.

(2) SOLID SOLUTIONS.

The temperature coefficient of solid solutions of good conductors is small in comparison with that of the constituents. In some cases it is nearly zero or even slightly negative. This agrees with the general statement on the relation between the sign of the temperature coefficient and the magnitude of resistance. Matthiesen's relation

$$\gamma R = \gamma^1 R^1.$$

also agrees with this statement. γ and R are the temperature coefficient and the resistance actually measured. γ^1 and R^1 are those calculated by the rule of averages from that of the components. This relation expresses that the higher the actual resistance as compared to the calculated one, the smaller the temperature coefficient.

The behavior of these solid solutions in the neighborhood of the absolute zero is not as yet known with certainty. It seems that at very low temperatures, say below 180° C., the restivity begins to drop fast and it is possible that at absolute zero it would be *nil*.

In solid solutions containing a "good" and a "poor" conductor,

or two "poor" conductors, the temperature coefficient has also a smaller absolute value than the components, this being in agreement with the fact that the resistance of the solid solutions is smaller than that of the constituents. Thus in case of boron, an addition of a small amount of carbon will decrease its resistance, but the rapidity with which this resistance decreases with the temperature is also greatly diminished.

(3) COMPOUNDS.

In compounds the sign of the temperature coefficient and its magnitude are also determined by the above rule. Good conductors among compounds have a positive temperature coefficient of resistance, but most compounds are poor conductors and therefore the temperature coefficient most commonly met with is negative. The relation between temperature and resistance is approximately linear in the case of good conductors, such as lead sulfide, and of an exponential nature in the case of the poor conductors.

Table VIII.

Conductivity of Pyrite		*Conductivity of PbS*	
Temp.	Res. in Ohms	Temp.	Res in Ohms
—180°	0.550	—180°	0.000885
—78	0.0251	—65	0.00157
—16.5	0.0239	0	0.00241
0	0.0240	18	0.00265
20	0.0240	104	0.00384
85	0.0279	140	0.00450
121	0.0300		
260	0.0357		
340	0.0388		

Table IX.

Conductivity of Magnetite		*Conductivity of Marcasite.*	
Temp.	Res. in Ohms	Temp.	Res in Ohms
15°	0.00794	—130°	>2600
150	0.00468	—78	242
226	0.00434	0	16.56
240	0.00435	16.7	10.25
280	0.00446	29	8.1
415	0.00820	65	4.68
470	0.01030	90	3.5
485	0.01120	150	2.2
		243	1.3

TABLE X.

Conductivity of CuO.		*Conductivity of Lime.*	
Temp.	Res. in Ohms	Temp.	Res. in Ohms
12	462400	763	70000000
59	91560	879	9125000
134	12360	930	4175000
157	5930	1011	2000000
268	556.5	1105	600000
463	36.3	1175	245500
487	27.8	1235	104100
691	2.34	1304	35100
873	.347	1370	2045
974	.121	1478	122.7
1038	.021	1468	91.0

Tables VIII, IX, X, contain measurements by Horton, Koenigsberger and others on the change of conductivity of a number of compounds with the temperature. In case of some of them, like magnesium oxide and quartz, a certain amount of electrolytic conduction must be assumed, and although the evidence is not sufficient it seems that the part of conduction which is of electrolytic nature increases with the temperature but assumes importance in most of these compounds only at temperatures very near the melting point.

PART II.

RELATIONS BETWEEN ELECTRICAL CONDUCTIVITY AND OTHER PHYSICAL PROPERTIES.

A. Electrical and Thermal Conductivity.

A striking parallelism is found between electrical conductivity and heat conductivity so long as one considers only a number of pure metals and a certain temperature interval. This parallelism is expressed by Franz-Wiedemann's law, complemented by Lorentz. This law is expressed by the formula

$$\frac{\text{Therm. Cond.}}{\text{Elec. Cond.} \times \text{Abs. Temp.}} = \text{Const.}$$

Table XI gives the thermal conductivity of different metals between —170 and 100° according to Lees, Jaeger and Disselhorst.

TABLE XI.

Heat Conductivity of Pure Metals at Different Temperatures According to Lees, Jaeger and Diesselhorst.

In gr. Cal. per cm.^{2} and 1° per cm.

Metal	-170 °C	-100 °C	$+18$ °C	$+100$ °C
Cu	1.112	0.973	0.916	0.908
Ag	0.996	1.008	0.974	0.992
Zn	0.280	0.271	0.268	0.262
Cd	0.240	0.231	0.217	0.216
Al	0.524	0.492	0.504	0.492
Sn	0.195	0.176	0.157	0.145
Pb	0.093	0.087	0.083	0.082

TABLE XII.

Ratio of Conductivities of Different Metals According to Jaeger and Diesselhorst.

Metal	Ratio	Temp. Coef.	Metal	Ratio	Temp. Coef.
Al	6.6×10^{10}	4.37	Sn	7.35×10^{10}	3.4
Cu	6.71×10^{10}	3.95	Pt	7.53×10^{10}	4.64
Ag	6.86×10^{10}	3.77	Pd	7.54×10^{10}	4.69
Au	7.09×10^{10}	3.75	Fe (1% C)	8.02×10^{10}	4.32
Ni	6.99×10^{10}	3.93	Bi	9.64×10^{10}	1.51
Zn	6.72×10^{10}	3.85	Constantan	11.06×10^{10}	2.39
Cd	7.06×10^{10}	3.73	Manganin..	9.14×10^{10}	2.74
Pb	7.15×10^{10}	4.07			

TABLE XIII.

Thermal and Electrical Conductivity of Al and Ni at High Temperatures.

Al.			Ni.		
Temp.	Ther. Cond.	Elec. Res.	Temp.	Ther. Cond.	Elec. Res.
0	0.47	3.	0	0.142	11
100	0.50	4.1	100	0.138	17
300	0.65	6.7	300	0.126	34
600	1.00	10.5	400	0.117	37
			500	0.103	40
			600	0.088	43.5
			700	0.070	47
			1200	0.058	(1100°—57)

Table XII gives the ratio of heat conductivity to electrical conductivity at ordinary temperature and the temperature coefficient of this ratio. It is seen that both the ratio at ordinary temperature and its temperature coefficient are nearly constant, and that the latter is nearly equal to 1/273.

When, however, attempts are made to apply this law to larger temperature intervals the discrepancy begins to be serious. Thus the variation of the ratio between the temperatures given above is, according to Lees, in some cases as much as 48 percent.

At high temperatures very few measurements of thermal conductivity have been made, but those that have been made do not agree with the requirements of the formula. Angell has made some measurements on aluminium and nickel. In the case of aluminium at higher temperatures the heat conductivity, in fact, increases, while the electrical conductivity, of course, decreases. In the case of nickel the course of the thermal conductivity is different from that of the electrical conductivity. It exhibits a critical point which the electrical conductivity does not show, and does not exhibit those critical points which are shown by the electrical conductivity. Nor does the law hold for all metals, bismuth forming a conspicuous exception. In solid solutions also the law does not hold.

Finally, in the case of poor conductors such as graphite, carbon, silicon and boron, the relation ceases to hold altogether, the thermal conductivity being thousands of times larger than it ought to be according to the electrical conductivity of the materials. This could be expected, since with insulators the thermal conductivity, far from being zero, has in some cases a magnitude equal to that of the lower members among metals.

Obviously, while the generalization of Franz-Wiedemann-Lorentz is significant, it must be considered as only a part of a broader generalization which is yet unknown.

B. Electrical Conductivity and Density.

The relation between electrical conductivity and the volume occupied by the substance is to my mind more significant than that between electrical conductivity and thermal conductivity.

We saw that at absolute zero the "good" conductors, the metals, have an infinite conductivity. The easiest way to account

for this is to assume that the matter of which the metals consist is in itself a perfect conductor and that the resistance of metals resides entirely in the gaps in its structure. At absolute zero, when the particles cease their agitation and come together, the resistance is zero. As the temperature rises and the metal expands, gaps appear between the particles and the resistance grows according to the way in which the insulating gaps grow. Both the resistance and the volume can be expressed as a parabolic function of temperature. The influence of temperature on the conductivity is accordingly, to a large extent, a volume effect. The resistance keeps on increasing until finally, at the melting point, with its sudden volume change, a sudden change of resistance also takes place, and, remarkably enough, with metals which expand on melting, the resistance increases and with metals in which contraction takes place (bismuth, antimony, gallium) the resistance decreases.

It seems that the co-volume (to use the usual expression), of the metal largely determines the resistance, although it is hard to tell which part of the resistance resides in the molecular co-volume, which in the atomic, and which in the space between the coarser molecular aggregates. From investigations of Broniewski it seems that metals can be classed in different groups, and that a certain group containing Ag, Au, Cu, K, Al, Pt, Pd, which the author considers as mono-atomic, shows a simple relation between the volume occupied and the resistance. For instance, the total atomic volume difference between the metal at absolute zero and the liquid at the melting point divided by the volume difference between absolute zero and the solid at the melting point, is in these metals very nearly 1.9 or nearly equal to the ratio of resistances of the molten and solid metal in the elements of this particular group, which could be investigated.

It seems, however, difficult to apply these speculations to other groups of metals and the actual relations will not be discovered until more is known about the molecular structure of solids.

Here, as in the parallelism between electrical and thermal conductivity, the "poor" conductors show different behavior. Their conductivity at absolute zero, when their density is highest, is zero, and from there on electrical conductivity and density change in opposite way. Shall one assume the existence of two kinds of

matter, one a perfect insulator and the other a perfect conductor, at absolute zero (Burton)? But this is speculation.

C. Electrical Conductivity and Hardness.

The close relationship between electrical conductivity and internal structure is shown in the parallelism between electrical conductivity and hardness. As a rule, poor conductors and insulators are found among brittle and hard materials while good conductors are usually soft and ductile. In metallic alloys this relation has been shown by Kurnakow to be of a quantitative nature, so much so that the curves connecting hardness with composition are in a number of alloys the exact counterpart of the curve of electrical conductivity. As an instance, I have drawn, together with the curve of electrical conductivity of gold-silver alloy, also the hardness curve. (Curve I, Fig. 1.)

The connection between optical properties and electrical conductivity lies outside the scope of this lecture.

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE ELECTRON THEORY OF METALLIC CONDUCTION.

By O. W. Richardson,
(Professor of Physics, Princeton University).

The view that the transportation of electricity in metallic conductors, like the corresponding phenomenon exhibited by electrolytes, is due to the motion of minute charged particles was a definite feature of the old Weberian formulation of electrodynamics. The modern development is due to the labors of Riecke, Drude, J. J. Thomson and others. According to the most prevalent form of the theory, and the one which we shall adopt, the atoms of the metal are regarded as continually dissociating into a negative electron and a positively charged residue. At the same time the electrons are constantly recombining with the positive residues. The electrons which escape from the atoms in this way are often called *free electrons.* Since the action by which they are liberated is exactly analogous to chemical dissociation, the state of equilibrium will be determined by laws analogous to those of mass action. On the simple theory which we have propounded, the rate of recombination will clearly be proportional to the number of free electrons present in unit volume. In the state of equilibrium the rate of recombination must be equal to the rate of dissociation; so that the number of free electrons per unit volume of the material will be definite at any given temperature.

There are good theoretical reasons for believing that the free electrons will behave very much after the fashion of the molecules of a gas. They will move about irregularly in all directions in the interior of the conductor with speeds which may be, and, on the average, are, very high. There is every reason to believe that they possess the same distribution of velocity as would an uncharged molecule of a gas of equal molecular mass, and that their mean kinetic energy is proportional to the absolute temperature. The law of distribution of speed and energy, in fact, is believed to be that which is associated with the name of Max-

well. We should rather expect that the atoms and positively charged residues would have an equal distribution of kinetic energy, but it is possible that they are jammed in some way which prevents this coming about. Whether the atoms and positive residues are able to move or not, they are to be regarded as only oscillating about fixed positions and not traveling from point to point of the material.

You are to remember that the mass, m, of the electrons is very small. It is only about 1/1800 of that of an atom of hydrogen. Their velocity of heat motion is therefore much greater than that of a molecule of a gas at the same temperature. The charge, e, which they carry is, however, equal to that which is associated with the liberation of an atom of hydrogen in electrolysis.

The effect of applying an electromotive force to a conductor which has the structure we have outlined is to superpose on the haphazard motion of the electrons which arises from thermal agitation, an average velocity of drift which, since they are negatively charged, is in the opposite direction to the applied force. This motion gives rise to the electric current which is thus entirely carried by the negative electrons.

One might, *a priori*, be tempted to suppose that the positive residues would also drift along under the influence of the electric field. If any such effect exists it must be extremely small. For, if it were appreciable, we should expect an electric current to transport atoms of one metal into another across the junction between the two metals. Careful experiments have been made by Riecke and others to detect such effects, but they have always led to negative results. This objection would be removed if we supposed that there were mobile positive particles of the same nature in different metals. There are, however, at least two serious objections to such a view. In the first place, no one has been able to demonstrate the separate existence of such particles, whereas the cathode rays, the negatively charged particles emitted from conductors under the influence of light and heat, the β rays from radioactive substances, the secondary Roentgen rays and the phenomena of ionization by collisions furnish us with direct experimental evidence of the occurrence of negative electrons, arising from every conceivable type of matter, and having an identical structure in all cases. In the second place, the hypothesis

of mobile positive electrons does not appear to be capable of removing such difficulties as are presented by the simpler theory.

The question of transportation of matter along with the electric current is the point at which conduction of the metallic type is most profoundly differentiated from electrolytic conduction. Although electronic conductivity exhibits its highest powers, as it were, in the pure metals, it is by no means confined to them. In my judgment, this type of conduction is exhibited by a large number of compounds, particularly oxides and sulphides at high temperatures, or at lower temperatures in the form in which they occur in minerals. On the other hand, a large number of fused salts exhibit typical electrolytic conductivity. It seems probable that it will not ultimately be possible to draw a sharp distinction between different materials in this respect. With further research we may expect to find substances in which the current is carried partly by electrons and partly by charged atoms, and other substances in which the current is carried mainly by electrons at some temperatures, while the transfer is mainly of the electrolytic type at others. There is some evidence that the conductivity of silicates and glasses generally is partly electronic and partly electrolytic, whilst Koenigsberger[1] has suggested that in the case of salts near the melting point there may be a gradual transition from the metallic conductivity which characterizes the solid at lower temperatures to the electrolytic conductivity of the fused salt.

At the outset I wish to avoid the appearance of attempting to create an impression that the electron theory of metallic conduction in its present state of development is able to furnish a simple and satisfactory explanation of all the phenomena exhibited by metallic conductors. We shall see that there are a number of experimental generalizations, some of them of a simple character, which it does not clearly foreshadow. Among these may be mentioned (1) the proportionality between the specific resistance of the pure metals and the absolute temperature, and (2) the absence of discontinuity in the thermoelectric power, to correspond with the discontinuity in the resistance, at the melting point of a metal. These *lacunæ* are, however, in all probability to be attributed to our ignorance of the molecular and sub-

[1] Jahrbuch der Radioaktivität und Elektronik. 4, 192 (1907).

molecular structure of the materials concerned rather than to anything defective in the electron theory as such. They are certainly offset by the surprising success that the theory has attained in other directions, for instance, in explaining the intimate relations between thermal and electric conductivity. The real strength of the theory does not rest so much on these triumphs in detail, important though they are, as on issues of a wider scope. There are a number of salient features of metallic conductivity for whose existence any other type of theory would appear to be incapable of accounting.

In addition to the absence of material transportation by the currents, the strongest arguments in favor of the electron theory of metallic conduction seem to me to be the following:

(1) Conductors when heated are found to emit negative electrons into the surrounding space.

(2) The typically good conductors are all metals, *i. e.*, they are electropositive elements whose atoms we should expect, on other grounds, to readily part with a negative electron.

(3) If the particles which carry the current did not possess an extremely small mass in proportion to their charge we should not expect to get the well-known effects produced by a magnetic field on electric currents in metals, *e. g.*, the change of resistance in a magnetic field and the Hall effect. These effects are unquestionably very complicated, and so far the electron theory has not been able to furnish an adequate quantitative explanation of them. On the other hand, it is the only theory which has been able to account for them qualitatively.

ELECTRICAL CONDUCTIVITY.

In order to illustrate the problem presented by electric and thermal conduction in metallic conductors we shall consider the behavior of the electrons to be much simpler than it is likely to be in any real case. The results of a more exact calculation will be given later. For the present we shall make the following assumptions: (1) That the electrons all move freely for the same distance, l, between two collisions, (2) that they all have the same velocity, v, of heat motion, and (3) that the motion of an electron subsequent to a collision is entirely independent of its history previous to the collision. We shall also assume that the

only force acting on the electrons throughout the free path, l, is the applied electric force, X. It follows from assumptions (1) and (2) that the "free" time, $t = \lambda/v$, which elapses between two successive collisions is the same for all the electrons. To be consistent with the requirements of the kinetic theory of matter, we take the kinetic energy, $1/2\ mv^2$, of the electrons to be equal to the mean value, $3/2\ R\theta$, of the same quantity for the atoms of a monatomic gas at the same temperature. Here θ is the absolute temperature, m is the mass of the electron, and R is the constant in the gas equation $pv = NR\theta$ where N is the number of molecules of gas to which this equation is applied. Subject to these simplified assumptions the electrical conductivity of a metal may be calculated as follows:

If e is the electric charge of an electron, the force acting on it during its free path is Xe, and its acceleration is Xe/m. If the component of the velocity of the electron parallel to the electric intensity at the beginning of the free path is u, the value of this component at the end of the free path will be $u + X\,e/m\,t$, where t is the free time. The speed with which the electrons carry the electric current will clearly be the average value of this component of the velocity during the free path for all the electrons which are present. Now, the average value of u is zero, since it is just as likely to be negative as positive, and the average value of $X\,e/m\,t$ is $1/2\,X\,e/m\,t$, since it increases uniformly from zero at the beginning of the free path to $X\,e/m\,t$ at the end. The average velocity of drift of the electrons in the direction of the electric field is thus $1/2\,X\,e/m\,t = 1/2\,X\,e/m\,l/v$. If n is the number of free electrons which are present in unit volume, the number of them which, in unit time, drift across a unit area drawn perpendicular to the direction of the electric force, X, will be $1/2\,n\,X\,e/m\,l/v$. Each of these carries a charge, e, so that the quantity of electricity transported across unit area in unit time, or, in other words, the electric current density, i, will be

$$i = \frac{n}{2}\,\frac{e^2}{m}\,\frac{l}{v}\,X = \frac{ne^2lv}{6R\theta}\,X$$

Thus the specific electrical conductivity, σ, is

$$\sigma = i/X = \frac{ne^2lv}{6R\theta} \qquad (1)$$

THERMAL CONDUCTIVITY.

Before discussing this formula in detail let us see if we cannot find an expression for the thermal conductivity of a metal. It is well known that the best conductors of electricity are also the best conductors of heat, so that it is natural to attempt to attribute the two effects to this same cause, *viz.*, the motion of the electrons. From this point of view the problem of the conduction of heat in a metal is the same as that in a gas having the same number of molecules in unit volume, the same free path and the same molecular weight and temperature as the electrons in the metal. This is only true provided we suppose that the amount of heat which is distributed by radiation and by the direct dynamical action of the molecular and positive residues on each other is negligible compared with that distributed by the rapidly moving electrons. The results can therefore only be expected to be true for good electrical conductors, since the worst electrical conductors have an appreciable heat conductivity which we certainly cannot attribute to the motion of electrons. Under these restrictions the problem of determining the thermal conductivity is mathematically identical with that of finding the thermal conductivity of the corresponding gas. This is a well known problem, the answer to which is given in any standard text-book on the kinetic theory of gases. In the notation we have already employed, the value of the specific thermal conductivity, k, is, in fact,

$$k = 1/2 \; nlv \; R \qquad (2)$$

Comparing this with equation (1) we see that

$$k/\sigma = 3 \frac{R^2}{e^2} \theta \qquad (3)$$

FORMULÆ GIVEN BY MORE GENERAL TREATMENT.

Formulæ (1), (2) and (3) have all been deduced on the basis of a special set of assumptions, as to the behavior of the electrons in the metal, which are much simpler than any likely to occur in nature. It is important to determine, if possible, those features of equations (1) to (3) which depend on the special assumptions rather than on the more fundamental lines of the theory. The

most satisfactory way of doing this is to carry out calculations of the same quantities in which the only assumptions made are of so general a character that, without knowing much about the behavior of the electrons inside the metal, we can feel fairly sure that they will cover all the possible eventualities. For example, we have good reason for believing that the free electrons do not all have the same velocity, as we have supposed, but have a distribution of velocity in accordance with Maxwell's law.[2] This distribution, moreover, is likely to be slightly disturbed when the metal is the seat of an electric intensity or a temperature gradient. An important advance was effected by H. A. Lorentz[3] when he showed how to calculate the slight change in the law of distribution of velocity which thus arises. His calculations, however, were restricted to the case in which the collisions of the electrons were like those which would occur if they encountered perfectly elastic immovable spheres. The writer succeeded[4] in showing that the same method could be applied on the much more general assumption that the collisions of the electrons took place with immovable centres of force, which varied as any power of the mutual distance. This extension has the great advantage that it enables us to do away with the idea of definite free paths and collisions and includes the case in which the electrons are never free from the action of appreciable forces throughout their motion. This, I think, is likely to be the case in nature. The more general assumptions that the electrons in the metal when in thermal and electrical equilibrium have Maxwell's law of distribution of velocity, and that the collisions are with immovable centres of force, varying as the s power of the mutual distance, lead to the following equations:

$$\sigma = \frac{e^2}{3\pi^{3/2} m^{1/2}} \frac{n}{N} (2R\theta)^{\frac{2}{s-1} - \frac{1}{2}} \frac{\Gamma\left(\frac{2}{s-1} + 2\right)}{K^{\frac{2}{s-1}} \int_0^\infty \sin^2 \theta \alpha \, d\alpha} \qquad (4)$$

[2] O. W. Richardson, Phil. Trans. A, **201**, 497 (1903). Phil. Mag. **16**, 915 (1908).
[3] Theory of Electrons, p. 266.
[4] Phil. Mag., **23**, 594 (April, 1912).

$$k = \frac{1}{12\pi^{3/2}m^{1/2}\theta}\,\frac{n}{N}\,(2R\theta)^{\frac{2}{s-1}+\frac{3}{2}}\,\frac{\Gamma\left(\frac{2}{s-1}+3\right)}{K^{\frac{2}{s-1}}\int_0^\infty \sin^2\theta\,\alpha\,d\alpha} \qquad (5)$$

$$k/\sigma = \frac{2s}{s-1}\,\frac{R^2}{e^2}\,\theta \qquad (6)$$

In these formulæ, N is the number of the centres of force per unit volume of the material, K is the strength of the centres (*i. e.*, the force on an electron at distance, d, is K/d^s, K being positive when the force is repulsive), $\Gamma(p)$ is $\int_0^\infty e^{-x}\,x^{p-1}\,dx$ and the integrals $\int_0^\infty \sin^2\theta\,\alpha\,d\alpha$ are functions of s only which may be evaluated when s is known. Formulæ identical with, or at any rate equivalent to, (4), (5) and (6) were first published by N. Bohr.[5]

COMPARISON WITH EXPERIMENT.

We are now in a position to discuss the different formulæ (1)-(6). The most striking fact about them is that, although, corresponding to the different suppositions on which the calculations are based, there is a considerable superficial difference between (1) and (4) and between (2) and (5); the difference between (3) and (6) is comparatively small. Each type of calculation leads to a relatively simple expression for k/σ, so that it seems fair to conclude that this ratio depends much less on the state of the electrons inside the conductor than either the electric or thermal conductivity separately.

This is in accordance with experimental requirements. About the middle of the last century Wiedemann and Franz stated as a conclusion from their experiments that the value of k/σ was the same for all the good conductors. Somewhat later L. Lorenz showed that this ratio was proportional to the absolute temperature. In more recent years our experimental knowledge of these quantities has been greatly increased by the more extensive experiments of Jaeger and Diesselhorst[6] and Lees.[7] The follow-

[5] Studier over Metallernes Elektron Theori. Afhandling for den Flosofiske Doktorgrad of Niels Bohr. Copenhagen (1911).

[6] Abhandl. der Physik. Techn. Reichsanstalt, **3**, 269, Berlin (1900).

[7] Phil. Trans. A, **208**, 381 (1908).

ing table gives the results of the measurements of the former observers:

Material	Ratio: Thermal Conductivity, Electrical Conductivity	Temperature Coefficient of this Ratio, Percent
Copper, commercial	6.76×10^{10} at 18° C.	—
Copper (1) pure	6.65×10^{10} at 18° C.	0.39
Copper (2) pure	6.71×10^{10} at 18° C.	0.39
Silver, pure	6.86×10^{10} at 18° C.	0.37
Gold (1)	7.27×10^{10} at 18° C.	0.36
Gold (2) pure	7.09×10^{10} at 18° C.	0.37
Nickel	6.99×10^{10} at 18° C.	0.39
Zinc (1)	7.05×10^{10} at 18° C.	0.38
Zinc (2) pure	6.72×10^{10} at 18° C.	0.38
Cadmium, pure	7.06×10^{10} at 18° C.	0.37
Lead, pure	7.15×10^{10} at 18° C.	0.40
Tin, pure	7.35×10^{10} at 18° C.	0.34
Aluminium	6.36×10^{10} at 18° C.	0.43
Platinum (1)	7.76×10^{10} at 18° C.	—
Platinum (2) pure	7.53×10^{10} at 18° C.	0.46
Palladium	7.54×10^{10} at 18° C.	0.46
Iron (1)	8.02×10^{10} at 18° C.	0.43
Iron (2)	8.38×10^{10} at 18° C.	0.44
Steel	9.03×10^{10} at 18° C.	0.35
Bismuth	9.64×10^{10} at 18° C.	0.15
Constantan (60Cu, 40Ni)	11.06×10^{10} at 18° C.	0.23
Manganin (84Cu, 4Ni, 12Mn)	9.14×10^{10} at 18° C.	0.27

It will be seen that for the pure metals there is very little difference in the value of the ratio, k/σ, and that the temperature coefficient of this ratio does not differ appreciably from the value 0.00366 called for by Lorenz's law. Let us see how the absolute magnitude of k/σ agrees with the theory.

Let us take formula (3), which gives the value of k/σ explicitly in terms of known physical quantities without any contingent element. To evaluate $3\frac{R^2}{e^2}\theta$ we may multiply top and bottom by n^2 where n is the number of molecules in a c.c. of a gas at 0° C. and 760 mm. Then nR is the value of R in the equation $pv = R\theta$ when p is in dynes per sq. cm. and $v = 1$ c.c. It is thus a well-known physical constant, and is equal to 3.72×10^3 ergs/deg. C. Now ne is evidently equal to the quantity of electricity required to liberate half a c.c. of hydrogen, measured under standard conditions, by electrolysis, since the molecule of hydrogen is diatomic. This is another well-known physical quantity, and is equal to 0.416 electromagnetic units. At 18° C. the value

of k/σ should therefore be equal to $3 \times \frac{(3.72)^2 \times 10^6}{(42)^2} \times 291$ $= 6.98 \times 10^{10}$ E. M. U. This is very close to the value to which the ratio tends for the pure metals. It must be admitted to be a remarkable result that the value of the ratio of the thermal to the electric conductivity can be calculated from the gas constant, the electrochemical equivalent of hydrogen and the absolute temperature, all of which are quantities which have apparently no special connection with the properties of metals.

It has been pointed out by Sir. J. J. Thomson that as the formula for k/σ does not contain m, the same result would be obtained whatever the mass of the carriers, so that this result cannot be taken as a *proof* that the current is carried by electrons. It may, however, be considered as confirmatory evidence of the truth of such a view.

Lees, who has made measurements of thermal and electric conductivity on the same samples of material down to the temperature of liquid air, found a continually increasing deviation from the laws of Wiedmann, Franz and Lorenz as the temperature was reduced. These deviations cannot be considered to be accounted for by the electron theory in its present form. The same is true of the sudden disappearance of electric resistance at the very lowest temperatures, which has recently been observed by Kammerlingh Onnes[8] in the case of mercury.

THE CENTRES OF FORCE.

If the results are to fit the more general theory, which is *a priori* more likely than that they should fit the more artificial simple theory, the experiments will have to accord with equation (6). This will be the case, as they agree with (3) if $2s/(s-1) = 3$, i. e., if $s = 3$. Thus the value of k/σ leads to the conclusion that the encounters of the electrons in the metal take place with immovable particles, which act on them with a force varying inversely as the cube of the distance. It is significant that, from an entirely different line of reasoning, Sir J. J. Thomson[9] has concluded that the collisions occur with centres of force having this distance law, which he finds to be necessary

[8] Electrician, **67**, 657 (1911).
[9] Phil. Mag., **14**, 217 (1907); **20**, 238 (1910).

if the electromagnetic temperature radiation (the so-called black body radiation) is to satisfy Wien's well-known law $E\lambda d\lambda = \lambda^{-5} F(\lambda\theta)\, d\lambda$. Thomson also shows that the strength, K, of the centres can, according to his theory of temperature radiation, be calculated from the values of the constants in Planck's radiation formula. In this way he finds $K = 2 \times 10^{-27}$. Let us compare this with the consequences of equations (4)-(6).

Since, from equation (6), we have been led to conclude that $s = 3$, everything which enters into (4) is known except $n/N.1/K$. We should expect that both n the number of current carrying electrons, and N the number of centres of force in unit volume, would be comparable with p the number of atoms of the conductor in unit volume. Thus if we put $n = \gamma p$ and $N = \delta p$, we should expect γ and δ to be comparable with unity. Substituting the specific electric conductivity of silver in (4), we find in the case of this substance that $\delta/\gamma K = 8.5 \times 10^{-26}$. This is of the same order of magnitude as the value of K given by Thomson's theory of radiation. If the two $K's$ are equal to one another, $\delta/\gamma = 42$ for silver, and, unless the number of current carrying electrons is much smaller than the number of atoms, each atom must provide a considerable number of the centres of force, which would therefore appear to be sub-atomic structures.

THERMIONIC EMISSION.

We shall now turn our attention to another group of phenomena displayed by conductors, *viz.*, the power which they have of emitting negative electrons. It is found that any substance when heated to an appropriate temperature acquires the power of discharging negative electricity without, in general, any corresponding power of discharging positive electricity. The carriers of this negative discharge are electrons, as was first shown by the experiments of Sir J. J. Thomson. This emission of negative electricity is a very rapidly changing function of the temperature and of such a nature that there is no definite temperature at which the emission begins. It is entirely a matter of the sensitiveness of the appliances used for measuring the currents. In the case of any substance it would, in all likelihood, be possible to measure these emissions at the very lowest temperatures if sufficiently delicate appliances could be obtained.

From the standpoint of the electron theory we may picture these effects in the following manner. We have seen that the interior of a conductor contains a large number of freely moving electrons. As these do not, for the most part, escape under ordinary conditions, there are evidently considerable forces at the surface tending to retain them in the interior. We have seen that, as the temperature of the metal is raised, the kinetic energy of the electrons is increased, so that we should expect some of them to gain sufficient kinetic energy at high temperatures to overcome these forces and so escape. This type of theory leads to formulæ which are in agreement with the facts and also with the considerations which follow.

Another way of looking at these questions is to regard the emission of the electrons as a process of evaporation of negative electricity from the conductors, just like the evaporation of steam from water. If the electrons are drawn away by an electric field the evaporation will go on continuously, but there will be a limit to the current which can be obtained in this way; this will be reached when all the negative electrons given off from the hot metal surface in a given time reach the opposite electrode in equal intervals of time. There is therefore what is known as a saturation current. If, however, the space above the hot surface is enclosed by an insulating boundary, the electrons will not be able to get away, and a state of affairs will soon be reached when as many electrons return to the surface from the space above as are emitted from it in a given time. There is thus an equilibrium concentration and pressure of the external electrons, which is determined by the nature of the metal and its temperature. Provided we can neglect the reflection of the electrons which return to the surface of emission, there is a simple connection between the number emitted by unit surface in unit time and the number in unit volume of the outside space in the state of equilibrium. For the condition for equilibrium is that the number emitted should be equal to the number returned, and the latter is equal to the number in unit volume of the space multiplied by the average value of the positive velocity component normal to the surface considered. If N is the number emitted and τ_0 the number in unit volume outside, the relation can, by a simple application of the kinetic theory, be shown to be

$$N = v_0 \left(\frac{R}{2\pi m}\right)^{1/2} \theta^{1/2} \tag{7}$$

Thus, if we can calculate the number v_0, we can readily deduce the value of the saturation current which is clearly Ne per unit area.

Now, from thermodynamic considerations similar to those made use of in calculating the temperature variation of the vapor pressure of a liquid, we can show that

$$v_o = Ae^{\int \frac{w}{R\theta^2} d\theta} = Ae^{-\frac{w}{R\theta} + \int \frac{1}{R\theta} \frac{\partial w}{\partial \theta} d\theta} \tag{8}$$

where A is a constant characteristic of the substance and entirely independent of θ, and w is the internal latent heat of evaporation of the electrons reckoned for a single electron. It follows from the combination of (7) with (8) that, if we may consider w to be independent of θ, the relation between the saturation current, i, and the temperature is given by an equation of the form

$$i = A_1 \theta^{1/2} e^{-b/\theta} \tag{9}$$

where A_1 and b are constants. We shall see later that w does depend on θ to a slight extent, and the effect of this is to change (9) to

$$i = A^1 \theta^p e^{-b^1/\theta} \tag{10}$$

where $A^1 p$ and b^1 are constants and p is very close to 2. As the term $e^{-b/\theta}$ varies very rapidly as θ changes, the difference between (9) and (10) is very small. The thermionic emission from a large number of substances has been found to be represented as a function of θ, by equation (9). So far as the writer is able to judge, (10) would do equally well if the constants were suitably adjusted. The experimental measurements of the variation of the emission with temperature are thus in satisfactory accordance with the theory.

There are some other consequences of this theory which are worthy of discussion. Since w is the internal latent heat of evaporation, the metal which emits the electrons will lose an amount of heat equal to w for each electron emitted. There will thus be a cooling effect when the electrons are allowed to escape from the metal. Experiments to measure this effect have been

made by Wehnelt[10] and his pupils, using a platinum wire covered with lime. These investigators have indeed found a cooling effect, but it appears to be larger than that called for by the theory. It would take too much space to discuss the possible reasons for this discrepancy. It may be that there is something exceptional about the behavior of lime in this respect, and it is also possible that the experimental arrangements used were at fault.

We should clearly also expect a heating effect when electrons are allowed to stream into a metal, corresponding to the heat liberated when a liquid condenses. This effect has been observed and measured by Richardson and Cooke[11] for a large number of metals. Considering the difficulty of these experiments, the results are in fair agreement with the theory.

Another consequence of this theory is that the distribution of velocity among the emitted electrons should be in accordance with Maxwell's law, and that their mean kinetic energy should be the same as that of a molecule of a monatomic gas which has the same temperature as the hot metal. These conclusions have been verified by a large number of experiments.[12]

There is an intimate connection between the emission of electrons by conductors and the phenomena of contact difference of potential and thermoelectric effects, as we shall now see.

CONTACT DIFFERENCE OF POTENTIAL.

Suppose that we have an enclosure provided with an insulating boundary maintained at a constant temperature, θ. The enclosure contains any number of different bodies, *A, B, C,* etc., of different materials and arranged in any manner. They may be supposed to be uncharged, to start with. Initially, some of them will give off more electrons than others, but this cannot go on indefinitely because those bodies which lose electrons, in doing so, become positively charged, and the field thus set up tends to prevent further loss. A steady state will ultimately be reached in which

[10] A. Wehnelt and F. Jentzsch, Ann. der Phys. **28**, 537 (1909). H. Schneider, Ann. der Physik, **37**, 569 (1912).

[11] Phil. Mag., **20**, 173 (1910); **21**, 404 (1911).

[12] Richardson and Brown, Phil. Mag. **16**, 353 (1908). Richardson, Phil. Mag. **16**, 890 (1908); **18**, 681 (1909).

each body loses as many electrons as it gains in unit time. In this steady state the bodies will have acquired electric potentials, V_1, V_2, V_3, etc. It can be shown that, if the suffixes m and p refer to the mth and pth bodies, respectively, then

$$V_m - V_p = 1/e(w_m - w_p) + {}_mP_p \qquad (11)$$

where ${}_mP_p$ denotes the Peltier heating effect due to the passage of unit quantity of electricity across a junction between conductors of the same materials as the mth and pth bodies, respectively. It can be shown that the differences $V_m - V_p$ are characteristic of the pairs of conductors and independent of their relative position. They are therefore true contact differences of potential.

Formula (11) is supported by the experiments on thermionic emission. Thus ${}_mP_p$ is always small compared with $\frac{w}{e}m$ or $w/e\,p$. For platinum w/e is about 5 volts, and for sodium a little under 3 volts. Thus sodium should be a little more than 2 volts electropositive with respect to platinum; this is close to the accepted value. According to this view, chemical action is quite unnecessary to account for contact difference of potential.

THERMOELECTRIC PHENOMENA.

Expressions for the different thermoelectric coefficients may be deduced in terms of the electron theory of conductors by considering the behavior of the surrounding atmospheres of electrons during certain simple thermodynamic cycles. If we wish to express the thermoelectric coefficients in terms of the number and state of the internal electrons it is necessary either to have some knowldge, or, in default of that, to make some hypothesis about the condition of the electrons inside a conductor. In the absence of definite knowledge it is desirable that any hypothesis made should be as general as possible, so as to cover any eventuality. On the other hand, it appears that all the thermoelectric coefficients can be expressed in terms of the intrinsic potentials, V_1, V_2, etc., the internal latent heats, w_1, w_2, etc., and the temperature, θ, without making any hypothesis as to the condition of the internal electrons.

THE THOMSON EFFECT.

We shall first consider the so-called "specific heat of electricity," σ. This may be calculated by considering the following cycle: Two conductors, A and A^1, of the same material are maintained at temperatures θ and θ^1. They are connected by a thin conductor, also of the same material. The atmospheres of electrons which surround A and A^1 are enclosed and separated from each other by a suitable insulating boundary. In general, the electric potentials of these electrons will not be the same, as the intrinsic potentials, V and V^1 of A and A^1, may be different on account of the difference in temperature. Let eV^1 be $>eV$. Then, if we surround A by a screen maintained at potential V^1 which will allow electrons to pass through it, for example, a wire gauze of indefinite fineness, the effect of this will be to change the potential of the electrons outside the screen to V^1 without altering their temperature or mean kinetic energy. It will, however, change their pressure in a way which can easily be calculated. The cycle consists in taking a given number of electrons out of the space outside of A at constant pressure, changing their temperature from θ to the temperature θ^1, characteristic of A^1, expanding at θ^1 to the pressure p^1 of the electrons around A^1, condensing in A^1 at constant pressure p^1 and then allowing the electrons to flow down the connecting conductor from A^1 to A. The electrons have thus been carried round a reversible cycle. The work and heat changes in all except the last process are obvious from the similarity with the evaporation of a liquid whose vapor is a perfect gas. The heat absorbed in the flow down the connecting conductor is, per electron, $e \int \sigma d\theta$. Thus it appears[13] that, by applying the equation $\int \frac{dQ}{\theta} = 0$ to the complete cycle, where dQ is the heat taken in at θ,

$$log\ p - \frac{\gamma}{\gamma - 1} log\ \theta + \frac{w}{R\theta} + \frac{e}{R}\int_{\theta}^{\theta} \sigma\ d\theta = A \qquad (12)$$

In this equation p is the pressure of the external electrons, γ is the ratio of their specific heats at constant pressure and at constant volume, A is a constant which is characteristic of the material

[13] Richardson, Phil. Mag., April 1912.

and which is independent of θ, and the other symbols have the meaning already given to them. Since

$$p = v_0 R\theta \tag{13}$$

it follows that

$$v_0 = A_2 e^{-\frac{w}{R\theta} + \int^{\theta}\left(\frac{1}{\gamma-1} - \frac{e\sigma}{R}\right) d\theta} \tag{14}$$

where A_2 does not involve θ. If there is to be no logical contradiction it is necessary that (8) and (14) should make v_0 identical functions of θ. This will only be the case provided

$$\frac{\partial w}{\partial \theta} = \frac{R}{\gamma - 1} - e\sigma \tag{15}$$

or

$$\sigma = \frac{1}{e}\left\{\frac{R}{\gamma - 1} - \frac{\partial w}{\partial \theta}\right\} \tag{16}$$

It thus appears that the specific heat of electricity, σ, is a function only of the universal constants, e, R and γ, and the rate of variation of the latent heat, w, with the temperature.

The value of γ is usually taken to be that which characterizes a monatomic gas, *viz.*, 5/3. At any rate, it cannot be greater than this. A calculation shows that $1/e\ R/\gamma\text{-}1$ is always larger and usually much larger than σ for the substances for which this quantity has been measured. It follows that $R/\gamma\text{-}1$ and $\partial w/\partial\theta$ have the same sign and are approximately equal in magnitude. If we put $\sigma = 0$ we have $\partial w/\partial\theta = R/\gamma\text{-}1$, which will probably be a satisfactory approximation in most cases. It leads to $p = 2$ in equation (10). This is clearly only an approximation, and, since σ is found in the case of most metals to vary in a rather complicated way with the temperature, it is not likely that (10) can be made an exact equation by any value of the index p.

THE PELTIER EFFECT.

The Peltier heating effect may be calculated by considering a cycle similar to that used in evaluating σ except that A and A^1 are now different materials and are at the *same* temperature. Since this thermodynamic cycle is isothermal there can be no

work done and no heat taken in on balance. These conditions lead again to equation (11) in another form, *viz.*:

$$ {}_mP_p = V_m - V_p - \frac{1}{e}(w_m - w_p) \qquad (11a) $$

As ${}_mP_p$, the Peltier heating effect at the junction between the *m*th and *p*th metals, is small compared with either V_m-V_p, the contact difference of potential, or $1/e\ (w^m - w_p)$, and as both these quantities are very susceptible to the influence of minute changes in the surfaces investigated, it would be very difficult to make a satisfactory experimental test of this formula.

THERMO-ELECTROMOTIVE FORCE AND THERMO-ELECTRIC POWER.

Having obtained expressions for the Peltier effect and the specific heat of electricity, the remaining quantities may be determined by means of the well-known principles introduced by Lord Kelvin into the theory of thermoelectric phenomena. Considering a circuit made of the two conductors designated by the suffixes m and p, and having junctions at θ and θ^1, respectively, the equation, the second law of thermodynamics, in the form

$$ \int \frac{dQ}{\theta} = 0, \text{ gives us } \frac{P^1}{\theta^1} - \frac{P}{\theta} + \int_\theta^{\theta^1} \frac{\sigma_m - \sigma_p}{\theta}\, d\theta = 0, \text{ whence} $$

$$ \sigma - \sigma_m = \theta \frac{\partial}{\partial \theta}\left(\frac{P}{\theta}\right) = \frac{\theta}{e}\frac{\partial}{\partial \theta}\left\{\frac{1}{\theta}[e(V_m - V_p) - w_m - w_p)]\right\} \qquad (17) $$

In combination with (16) this gives

$$ \frac{w_m}{e} - \frac{w_p}{e} = V_m - \theta \frac{\partial V_m}{\partial \theta} - \left(V_p - \theta \frac{\partial V_p}{\partial \theta}\right) \qquad (18) $$

By the principle of the conservation of energy, the maximum work done by the thermoelectric circuit is equal to the net amount of heat taken in reversibly, so that, if T is the thermoelectromotive force,

$$ Te = Pe^1 - Pe + e\int_\theta^{\theta^1} (\sigma_m - \sigma_p)\, d\theta \qquad (19) $$

$$ = \int_\theta^{\theta^1} \frac{e\,(V_m - V_p) - (w_m - w_p)}{\theta}\, d\theta \qquad (20) $$

by virtue of (11) and (17), also from (19) combined with (16)

$$T = V_m^1 - V_p^1 - (V_m - V_p) \tag{21}$$

For the thermoelectric power $\partial T/\partial\theta$ of the circuit we evidently have, by differentiation of (20) and (21), the two equivalent expressions:

$$\frac{\partial T}{\partial\theta} = \frac{e\,(V_m - V_p) - (w_m - w_p)}{e\theta} \tag{22}$$

and

$$\frac{\partial T}{\partial\theta} = \frac{\partial}{\partial\theta}(V_m - V_p) \tag{23}$$

Thus, according to the present theory, the thermoelectric power of any circuit is determined entirely by the temperature coefficient of the contact difference of potential of the metals concerned. The Thomson coefficient, σ, on the other hand, depends solely on the temperature coefficient of the latent heat of evaporation of the electrons from the metal in question.

GENERAL CONSIDERATIONS.

It will be observed that all the relations (11) and (12) to (23) are entirely independent of any assumption as to the condition of the electrons inside the conductor. They are based solely on the following hypotheses:

(1) That thermoelectric phenomena are thermodynamically reversible in the sense used in Kelvin's theory.

(2) That, for some reason, conductors emit electrons without otherwise undergoing change in their material nature and consequently the external electrons have an equilibrium pressure, which is a function of the temperature.

(3) That the external electrons obey the gas law $p = v_0 R\theta$ when they are sufficiently dilute.

If any of the relations (11) and (12) to (23) can be shown to be really inconsistent with the results of experiment, it would follow that one or more of the three hypotheses must be at fault. It is unlikely that (1) and (3) are untrue, so that (2) would probably have to bear the burden. If (2) could be shown to be false it would follow that not only thermionic emission, but

also photoelectric emission, of electrons must be conditioned by material changes of chemical or radioactive type, in every case in which such emission occurs. In the light of the present experimental evidence this must be regarded as extremely improbable.

Formulæ for the thermoelectric quantities in terms of the internal electrons can readily be obtained if we make some hypothesis about the state of the electrons inside conductors. Such formulæ have been given by different writers and naturally depend on the hypotheses made. As they are not at present within the range of experimental enquiry, I shall content myself with referring to two papers in which such formulæ are discussed.[14]

THE CONDUCTING ELECTRONS.

The most general of the expressions just referred to, which have been obtained for the various thermoelectric quantities, involve integrals which are extended over all the electrons which are able *at any time* to take part in thermoelectric phenomena. In general, we should expect only part of these electrons to be capable of engaging in the transportation of the electric current. Many of them will be so strongly attached to the atom nearest them that they will only rarely be able to escape from its immediate neighborhood. Such electrons will only be slightly displaced under the influence of an external field, and will not participate in the conveyance of the conduction current.

It seems natural to suppose that the conduction current is carried by those electrons of the class contemplated which are instantaneously executing open (as opposed to closed) orbits. An expression for the number, N, of electrons which are executing open orbits may be obtained on the assumption (which accords with our previous conclusions) that the electrons are attracted by centres of force varying inversely as the cube of the mutual distance. It may then be shown to follow from the laws of central orbits that the condition that an orbit should be open is that the kinetic energy of the particle, at any point, should exceed the energy which it would acquire by falling from infinity to that point, under the action of the central force. It follows from the kinetic theory of matter that the instantaneous kinetic

[14] O. W. Richardson, Phil. Mag., Feb. and April, 1912.

energy of the electrons at any point is independent of their potential energy at that point. These two results enable the number of current carrying electrons at any point and also the number, n, of them in unit volume to be calculated. Thus I find that

$$n = n_0 \int_T X\left(\frac{\varphi}{R\theta}\right) e^{\varphi/R\theta}\, dT \Big/ \int_T e^{\varphi/R\theta}\, dT \qquad (24)$$

where

$$X\left(\frac{\varphi}{R\theta}\right) = \frac{2}{\sqrt{\pi}} \left\{ \sqrt{\frac{\varphi}{R\theta}}\, e^{\varphi/R\theta} + \int^{\infty} \left(\frac{\varphi}{R\theta}\right)^{1/2} e^{-x^2} dx \right\} \qquad (25)$$

In these expressions n_0 is the total number of electrons which can become free in unit volume, T is the total volume of the conductor, and φ is the potential energy of an electron at the element of volume dT.

It is impossible to make any very precise deductions about the behavior of integrals like those in (24) without going more definitely than we have done into the distribution of the potential energy, φ, about the volume, T. We can, however, draw some very general conclusions. The chief factor which determines wide variations of the conductivity of substances is almost certainly n, the number of current carrying electrons in unit volume. Now, according to (24), n is a function only of the distribution of $\varphi/R\theta$ about the space, T, of the conductor. The writer[15] has shown that the thermoelectric quantities can also be expressed as functions of the spacial distribution of this same quantity $\varphi/R\theta$. We should therefore expect that any change which produced a *continuous* variation in the conductivity would produce a corresponding change in the thermoelectric properties of the material. Without being able to specify the precise nature of the correlation, we should expect the two properties to vary together in a corresponding manner.

This is well exemplified in the behavior of alloys. These are found to behave quite differently according to whether they are solidified solutions or merely mixtures of crystals. The phenomena are somewhat complicated in cases where the solubility only occurs up to certain limits or where chemical compounds are

[15] Phil. Mag., April, 1912.

formed. These effects, however, only increase the number of constituents which have to be considered; the main question from the electrical standpoint appears to be whether the constituents are mutually soluble or not. Where the constituents are mutually insoluble and the alloy is a mixture of different crystals, its conductivity can be calculated from the conductivities of the constituents by simply multiplying by the proportions in which they occur and adding the results together. The conductivity is thus a linear function of the percentage composition. In such cases, precisely the same thing is true of the thermoelectric power of the alloy in a circuit containing some standard metal.

The behavior of alloys in which the constituents are mutually soluble is entirely different. The addition of a small quantity of either constituent to the other pure metal produces a large diminution in the specific electrical conductivity. The diminution produced by the addition of a given quantity of the foreign substance diminishes progressively as further amounts are added. Thus the curve which expresses the conductivity as a function of the percentage composition drops sharply from the value corresponding to either pure metal, and has a flat minimum between these two values. In these cases the curves which express the thermoelectric powers as functions of the composition are entirely similar in character.

There is one instance in which a considerable change in electrical conductivity is unaccompanied by change in the thermoelectric quantities, *viz.*, in the case of the pure metals at the melting point. The change here, however, is a sharp one and is not necessarily incompatible with the equations referred to. The above would, nevertheless, be difficult to reconcile with the formulæ obtained by various writers, on the explicit or implicit assumption that the internal electrons can be treated as though they executed free paths, practically free from force. This change can therefore be regarded, as Sir J. J. Thomson[16] has pointed out, as a practically insuperable objection to such a simple theory. It seems probable that there is something in the conditions of equilibrium at the melting point which makes the thermoelectric power take the same value for the solid and liquid phase.

[16] The Corpuscular Theory of Matter, p. 76, New York (1907).

Although I have not yet succeeded in doing much with equation (24) in the general case, it is worth while to consider its behavior in one or two special cases. In the case of poor conductors there are presumably very few current carrying electrons, so that we should expect $\varphi/R\theta$ to be large. If, for the sake of illustration, we make $\varphi/R\theta$ large and constant throughout an appreciable fraction of T in (24), we find

$$n = n^0 \frac{2}{\sqrt{\pi}} \left(\frac{\varphi^2}{R\theta}\right)^{1/2} e^{-\varphi/R\theta}. \qquad (26)$$

This formula makes n, and therefore the electric conductivity also, vary very rapidly with θ, on account of the factor $e^{-\varphi/R\theta}$. The experiments made by Horton,[17] Koenigsberger[18] and others on the conductivity of comparatively poor conductors show that the temperature variation can be represented satisfactorily, over a considerable range, by a formula for the conductivity developed from an expression for the number of current carrying electrons, of the type of (26).

In the second place, suppose $\varphi/R\theta$ to be small. Then, if we neglect terms involving $\left(\frac{\varphi}{R\theta}\right)^{5/2}$ and higher powers, we find

$$n = n_0 \left(1 - \frac{4}{3\sqrt{\pi}} (R\theta)^{-3/2} \varphi_1^{3/2}\right) \qquad (27)$$

where $\varphi_1^{3/2}$ is the mean value of $\varphi^{3/2}$ taken throughout the volume of the conductor. We should expect this type of formula to apply, qualitatively at least, to the best conductors, for the variation of conductivity with temperature, in such cases, is comparatively small. According to (27), n will always be less than n_0, which it approaches asymptotically as $\varphi/R\theta$ approaches zero. In order to explain the decrease in the conductivity of the pure metals with rising temperature it is necessary (if this theory is to hold) to fall back on an increase either in the number of the centres of force per unit volume or an increase in their strength.

Some of the rather poor conductors investigated by Koenigsberger[19] exhibit very interesting phenomena. Thus, in the case of magnetite the conductivity increases rapidly with increasing

[17] Phil. Mag., **11**, 505 (1906).
[18] Ann. der Phys., **32**, 179 (1910).
[19] *Loc. cit.*

temperature, at low temperatures, to a maximum at about 240° C. After that it falls off as the temperature rises in a manner which resembles the behavior of the metals. The rapid increase at low temperatures is evidently due to the large increase of n with θ when $\varphi/R\theta$ is large. The subsequent decrease may tentatively be attributed to an increase in the number of the repelling centres or to a change in the magnetic structure of the substance.

MAGNETIC EFFECTS.

These effects, *viz.*, the Hall effect, the change of resistance in a magnetic field, the Kerr effect and the thermomagnetic phenomena, are very complex, and the electron theory has only been able, as yet, to offer a partial explanation of them. One of the important factors in causing them is the deflection of the paths of the electrons causd by the application of a magnetic field. This, however, is only part of the story, since it would lead to a Hall effect, for example, in the same direction in all metals, whereas it is found that the direction of the Hall effect is not invariably the same. It is probable that a complete explanation of these effects will have to take into account a number of other factors of which the following suggest themselves: (1) Changes in the orientation and structure of the atoms produced by the magnetic field; (2) effects arising from the presence of polarization electrons; and (3) changes in the number of current carrying electrons caused by the magnetic field. These are phenomena about which little is really known, and, in any event, it would exceed the limits of this discussion to enter into their possible bearing on the phenomena considered.

In addition to the papers referred to, the reader who wishes to pursue this subject further will find the following works of reference useful:

J. J. Thomson. The Corpuscular Theory of Matter. New York, Charles Scribner's Sons, 1907

H. A. Lorentz. The Theory of Electrons. Leipzig, 1909.

K. Baedeker. Die Elektrischen Erscheinungen in Metallischen Leitern. Fr. Vieweg und Sohn, Braunschweig, 1911.

J. Koenigsberger. Stand der Forschung über die Elektrizitätsleitung in festen Körpern und ihre Beziehung zur Elektronentheorie. Jahrbuch der Radioaktivität und Elektronik, **4**, 158 (1907).

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE ELECTRIC CONDUCTIVITY OF PURE LIQUIDS.

By Stewart J. Lloyd.

The purpose of this symposium, as I take it, is to present first an accurate statement of the facts which are known as to the conduction of electricity under any and all circumstances, and secondly, by comparing the theories advanced to account for the facts in different cases, to see if some common ground cannot be found on which all cases of electrical conductivity may stand. The present paper, therefore, as a contribution to this end, consists of a statement of what is known as to the electrical conductivity of pure liquids, how it varies with the temperature, its relation to viscosity, whether pure liquids are decomposed according to Faraday's law, etc., followed by a statement of the theory put forward to correlate these facts, and to connect them with what is known of conductivity in solutions of all kinds, in gases and in solids. It does not contain any new experimental work by the author.

Of the three classes of conductors into which pure liquids may be divided, that of the electrolytic conductors is by far the most interesting, and will be dealt with here at greatest length. Inasmuch, also, as the only pure liquids in this class that show a marked conductivity are the "fused salts," and since practically all the literature on the electrical behaviour of these fused salts, up to 1905, is collected in Lorenz's monograph on that subject, a great deal of what is given here has been taken from that admirable work.[1]

Those of us who, like myself, were brought up under the shadow of the electrolytic dissociation theory, and hence in the tacit belief that the study of dilute aqueous solutions comprised the greater part of chemistry, may possibly have found the idea

[1] Die Elektrolyse geschmolzener Salze. R. Lorenz.

of pure liquids possessing a high degree of electrolytic conductivity somewhat strange. Electrolytic conductivity was invariably associated with solutions, with something dissolved in something else, usually water, the implicit inference being, of course, that the presence of a solvent was necessary to produce ions to carry the current. The fact that the conductivity of water, alcohol, ether, and other common liquids diminished steadily as purification reduced the amount of dissolved foreign matter present, and also that low conductivity was, and is, used as a criterion of purity for a liquid,[2] naturally tended to sustain the idea that all pure liquids were more or less insulators. Indeed, the average textbook of electrochemistry today is apt to leave the student with a mistaken idea as to the relative conducting power of aqueous solutions and pure fused salts.

The technical importance of the processes utilizing electrolytic conduction in pure liquids, that is in pure fused salts, is, at least, one very cogent reason for their study. The production of sodium and potassium from the fused hydroxides, by Castner's method, the Acker process for obtaining sodium from fused salt, and the production of calcium from the chloride are of interest in this connection. Further, from the pure fused salts one passes naturally to the fused solutions which are of even more technical interest. It would naturally be expected, also, that the study of pure conducting liquids would lead to results of importance from the theoretical side. Since there is only one substance involved, the complications attending conductivity in solutions would naturally be absent, so that we might have reason to expect that the phenomena of conductivity in pure liquids would be most apt to give us the clue to the mechanism of electrolytic conductivity in general.

Pure liquids, it appears, must be divided into three classes as regards their conduction of electricity; into metallic conductors, such as mercury and the other metals when in the liquid state; electrolytic conductors, of which the fused salts are the type, and liquids which, though practically insulators, have been shown to possess the conducting properties of a dense gas.

Of the pure liquids exhibiting metallic conductivity little need

[2] McIntosh, Trans. Chem. Soc. **86**, 1899 (1904). "The purity of the solvent was established by measuring its resistance."

be said, especially as this type of conduction has been treated fully by others at this time. Of mercury alone has the conductivity been carefully measured. A few measurements at various temperatures have been made by De La Rue, Vassura, Bernini, Northrup and others on the following metals when liquid: sodium, potassium, caesium, lithium, thallium, zinc, cadmium, lead, tin, antimony, bismuth, and gallium.[3]

Their specific conductivities in reciprocal ohms are:

	Temp. C°	
Bismuth	271	0.781×10^{4}
	358	0.737×10^{4}
Antimony	860	0.822×10^{4}
Cadmium	318	3.79×10^{4}
Caesium	24	2.54×10^{4}
	44	2.32×10^{4}
Gallium	240	1.22×10^{4}
Lithium	230	2.35×10^{4}
Lead	327	1.04×10^{4}
	358	1.04×10^{4}
	860	0.81×10^{4}

	Temp. C°	
Potassium	100	5.04×10^{4}
Sodium	100	4.3×10^{4}
Tin	226.5	2.11×10^{4}
	358	1.96×10^{4}
	860	1.48×10^{4}
Thallium	294	1.35×10^{4}
Zinc	420	2.71×10^{4}
	440	2.69×10^{4}

As everyone knows, the conductivity of metallic conductors decreases with the temperature. It is interesting to note that the passage from the solid to the liquid state is accompanied by a sharp drop in the conductivity in all cases that have been measured except three. Upon melting, tin rises in resistance 10 percent, cadmium 30 percent, zinc 100 percent, lead 90 percent, sodium 44.8 percent, potassium 52.2 percent. Antimony on the other hand decreases its resistance 29 percent, bismuth over 50 percent, and gallium 41.0 percent.

There does not appear to be any record of a liquid other than a metal exhibiting metallic conductivity. The apparent exceptions to this rule, namely fused lead fluoride, silver sulphide, and a few other fused salts have been shown upon careful examination to conduct electrolytically.

It is rather remarkable that more measurements of the electrical conductivity of molten metals have not been made. They are urgently needed in view of the amount of high temperature research now in progress, especially that having to do with induction furnaces. Now that methods of measuring high tempera-

[3] Landolt and Börnstein. Tables, p. 254, Vol. I.
Northrup, Trans. Am. Electrochem. Soc. **20**, 185 (1911).

tures have been so greatly improved there is no reason why such data should not be secured.

Of little practical importance, but of considerable scientific interest is the discovery by Jaffé[5] that certain poorly conducting liquids really behave as dense gases, so far as conductivity is concerned. Pure hexane, for instance, when very carefully purified, shows a pronounced saturation current. The rate of recombination of the ions produced in liquid hexane by radium was measured by precisely the same methods as are employed in the case of gases. The method of purification adopted by Jaffé for hexane, namely the application of large electromotive forces for a long period, when applied to ethyl ether[6] and to liquid sulphur dioxide,[7] also made apparent the existence of a saturation current. This fact, that the conductivity of some pure liquids, even of one with so high a dissociating power as sulphur dioxide, does not conform to Ohm's law, and hence that what little conductivity it shows is not due to electrolytic dissociation, is very interesting and suggests that possibly the same may be true of water.

ELECTROLYTIC CONDUCTIVITY OF PURE LIQUIDS.

When we come to consider the electrolytic conductivity of pure liquids, the remarkable fact noticed long ago by Kohlrausch confronts us, that at ordinary or low temperatures there is no pure liquid known which exhibits good or even fair electrolytic conductivity. Water, alcohol, bromine, iodine, sulphur, sulphur dioxide, the liquified halogen hydrides, pure sulphuric acid, and the numberless organic liquids examined by Walden,[8] Kahlenberg, Lincoln[9] and others, are all exceedingly poor conductors. Nor, indeed, are the few inorganic salts which are liquid at ordinary temperatures any better. The chlorides of antimony, stannic chloride and arsenic chloride do not conduct, while the chlorides and oxychlorides of phosphorus though examined up to their boiling points show no signs of becoming conductors.

On the other hand, when our common salts, bases and oxides,

[5] Ann. Physik **28**, 326-70; **82**, 146. Physik. Zeit. **11**, 571.
[6] Schroeder, Ann. Physik. **28**, 503.
[7] J. Carvallo. Compt. rend. **151**, 717-9.
[8] Zeit. Phys. Chem. **10**, 563 *et seq.*
[9] J. Phys. Chem. **5**, 339 *et seq.*

are raised to temperatures around their melting points, practically all of them become conductors, and most of them very good conductors. The exceptions to this rule are remarkably few. The following do not appreciably conduct: beryllium chloride, aluminium bromide, yttrium chloride, titanium chloride, zirconium chloride, thorium chloride, mercuric chloride, mercuric bromide, mercurous chloride, mercuric iodide, germanium chloride, stannic iodide, the sulphides of arsenic, the bromides of antimony, the iodides of antimony, the chlorides and oxychlorides of vanadium, selenium chloride, chromium chloride and oxychloride, molybdenum and tungsten chlorides, osmium oxide, bismuth oxide, and boric acid. What few organic salts have been measured in the fused condition conduct. Oxy-benzoic acid does not. Practically the only *common* fused salt that does not conduct is mercuric chloride.[10]

Despite the number of measurements that have been made of the conductivity of fused salts, the data on record are exceedingly discordant, a fact which is doubtless due to the difficulty of maintaining and measuring temperatures well above the ordinary.

What are the experimental data with regard to the electrolytic conductivity of pure liquids?

The two cases referred to above may be distinguished as: First, the very slightly conducting substances which are liquid at ordinary temperatures, such as water, and second, the fused salts, using the word salt in the broad sense.

So slight is the conductivity of members of the first class that exceedingly little information has been accumulated concerning them. Water alone has been studied with care. Its conductivity has been measured by Noyes up to a temperature of 306° C.[11] Naturally the conductivity continually rises as is shown by the following figures, where it is given in reciprocal ohms:

26°	140°	218°	306°
1.25×10^{-6}	4.55×10^{-6}	6.5×10^{-6}	7.3×10^{-6}

The relation between conductivity and viscosity, density, etc., has not been examined for any liquid of this class.

Experimental data on the behaviour of fused salts have been

[10] Lorenz. Vol. II, p. 184.
[11] Carnegie Institution. Bull. 63, p. 39.

accumulated by many observers, including Faraday, Foussereau, Grätz, Lorenz and Goodwin. The main results only, with occasionally an outline of the evidence, will be given here.

How does the conductivity of pure fused salts vary with the temperature? Investigations on this point have been made by Poincaré, Braun, Kohlraush, Foussereau, Grätz, Lorenz and Goodwin.[12] In general it appears that the conductivity steadily increases with the temperature, but that the relation is by no means a linear one. The temperature coefficient of the conductivity of molten salts is much less than that of aqueous solutions. Silver nitrate, for instance, at 272° has a conductivity of 0.970. At 375° its conductivity is 1.32, an increase of 35 percent. Of the many formulas proposed to express the relation between conductivity and temperature for all salts, none has any general validity.

How does the conductivity of fused salts vary with the density? Poincaré has examined this point carefully, and has obtained a remarkable empirical equation connecting the conductivity at any temperature with the expansion coefficient of the liquid, so that a knowledge of the density of the liquid at any temperature will, with the aid of the constants of the equation, give its conductivity.

$$L = Ke^{A\left(T + \frac{b}{2}T^2\right)}$$

in which,

L is the conductivity.
A is a constant.
b is the expansion coefficient.
T is temperature (absolute).

This formula has not, however, been tested by others.[13]

Recently, also, the densities of some five salts have been very carefully investigated by Goodwin and Mailey.[14] No linear relationship between density and conductivity was observed.

What is the relation between conductivity and viscosity, or fluidity?

Fossereau[15] concluded from measurements on potassium

[12] Lorenz. Vol. II, p. 200.
[13] Phys. Rev. **25**, 469-89; **26**, 28-60.
[14] Trans. Am. Electrochem. Soc., **11**, 211-23 (1906).
[15] Lorenz, Vol. II, p. 198.

chlorate, sodium nitrate, potassium nitrate, ammonium nitrate, and mixtures thereof, that the specific conductivity for any liquid was directly proportional to its fluidity, but that no simple relation existed between the fluidity and conductivity of different salts. Goodwin and Mailey,[14] on the other hand, found as a result of an elaborate series of measurements on five salts that Foussereau's generalization did not hold, but that the *equivalent* fluidity was, within the limits of experimental error, proportional to the *equivalent* conductivity, a result confirmed by Lorenz and Kalmus.[17] The ratio, equivalent conductivity to equivalent fluidity, however, tended to decrease with rise of temperature, from which fact interesting theoretical deductions were drawn by the authors. Experiments by Arndt[16] on sodium metaphosphate dissolved in boric anhydride confirm Goodwin's results.

Is the passage from solid to liquid accompanied by an abrupt change in the conductivity, as is the case with metals?

The conclusions reached on this point by the two investigators who have studied it are directly opposed. Foussereau[15] found a great difference in conductivity in the range of a few degrees around the melting point. As he did not believe that sharp melting points existed, he did not attempt to make measurements at the exact melting point. He found, for example, that potassium chlorate at 352° (solid) has a specific resistance of 79,800; at 359° (liquid) a specific resistance of 4.19.

Sodium nitrate, potassium nitrate, ammonium nitrate, gave similar ratios, while zinc chloride, solid at 240°, with a resistivity of 139, is liquid at 258° and has there a resistivity of 4.47.

Grätz,[18] on the other hand, examining stannous chloride, cadmium chloride, zinc bromide, lead iodide, and potassium nitrate, found that only in exceptional cases was the melting point a point of discontinuity. It appears, as a matter of fact, that every kind of behavior is shown, from one extreme to the other, depending upon the particular salt used.

Can we predict, from a knowledge of the conductivity of a salt in aqueous solution, whether or not it will conduct well when fused?

[16] Berichte, **40**, 2937-40.
[17] Zeit. Physik. Chemie, **59**, 17.
[18] Lorenz, Vol. II, p. 219.

There does not appear to be any relationship whatsoever between conductivities in the fused state and those in aqueous and other solutions. Some salts which conduct well when fused are very poor conductors when dissolved in water, and *vice versa.* It is worthy of note, however, that mercuric chloride, a non-conductor when fused, is practically a non-conductor in aqueous solution.

Does Faraday's law hold for fused salts? Extended investigations by Lorenz and others have definitely settled this point in the affirmative.

The phenomena of polarization, the existence of definite decomposition voltages, varying markedly with the temperature, and the possibility of constructing galvanic elements with fused electrolytes have all been shown. It has also been found impossible to predict the conductivity of mixtures of fused salts from measurements on the individual substances, though, in general, mixtures have a greater conductivity than would be calculated by simple proportion.

These are, in outline, the experimental data with regard to the conductivity of fused salts. What is the accepted opinion as to the mechanism of conductivity in these cases? Is the theory of electrolytic dissociation, which has served so well for dilute aqueous solutions, capable of describing and correlating these phenomena? The general opinion of those who have done experimental work in this field appears to be that it is, indeed, most of them have really taken it for granted, and interpreted their experimental results accordingly.

The experimental evidence in favor of assuming the existence of dissociation in fused salts has been summed up by Lorenz.[19] We have the same products of electrolysis as in aqueous solutions, the same ion going to the cathode, the same to the anode. Faraday's law holds good, and the same amount of electricity is associated with a gram equivalent, 96,540 coulombs. Polarization, separation of metals by varying voltage, and indeed almost all the phenomena accompanying conductivity in aqueous solutions can be shown with fused salts.

If, however, we assume that pure liquids that conduct well are highly dissociated, as we believe good conductors in aqueous

[19] Lorenz. Vol. III, p. 288.

solution to be, we must ask ourselves at once, just what means we have of measuring the exact extent to which the dissociation is carried. If, for instance, fused sodium chloride is broken up partially into ions, sodium and chlorine, does the undissociated part constitute 10 or 90 percent of the whole, and what is the effect of temperature on that proportion? Obviously the methods used will have to be very different from those used for aqueous solutions.

It may be said at once that direct methods, that is, methods which deduce the degree of dissociation of pure fused salts from their properties and behavior when pure and not dissolved in some other fused substance, are practically non-existent, those that have been applied resting on some very doubtful assumption. For example, Abegg[20] has calculated the dissociation of silver chloride on the assumption that the decomposition voltage of an ion is independent of the solvent from which it separates. Similar calculations have also been made by Lorenz,[21] using, however, the lead chloride cell to obtain some of the necessary data.

The conclusion that fused salts are very highly dissociated has been drawn by several investigators from the relation existing between conductivity and viscosity. Since equivalent conductivity is very closely proportional to equivalent fluidity over a wide range of temperature, the conclusion was drawn that the change in conductivity was entirely accounted for by the change in fluidity, hence that the degree of dissociation did not change materially, and hence that the dissociation was almost complete at all temperatures. Goodwin and Mailey,[22] from their experiments on the relation between conductivity and fluidity, in which the ratio between the two decreases slightly at high temperatures, conclude that the dissociation even decreases with rise of temperature, a behavior like that shown by pure water.

Additional evidence concerning the degree of dissociation of fused salts has been adduced from molecular weight measurements, using other fused salts as solvents, and from conductivity measurements in which a non-conducting fused solvent was used. Foote and Levy[23] have measured the molecular weight of various

[20] Zeit. Electrochemie, **5**, 353 (1899).
[21] Lorenz, Vol. III, p. 304.
[22] Trans. Am. Electrochem. Soc. **11**, 211-23 (1906).
[23] Am. Chem. Journal **37**, 494.

sodium and chlorate salts in fused sodium chlorate. Sodium chlorate is a good conductor when fused, hence we should expect it, the solvent, in this case, to be itself dissociated. Normal molecular weights were found in every case. An ingenious method of calculation is used to show that this is to be expected if both solvent and solute are practically completely dissociated. Mercuric chloride, however, is one of the very few non-conducting fused salts, therefore, presumably, is undissociated. Alkali chlorides dissolved in mercuric chloride have also normal molecular weights, that is weights corresponding to the full undissociated molecule.[24] Likewise they conduct well. Here an appeal is made to a supposed complex with the solvent to account for the molecular weights and the conductivity.

Recent works by Sackur[25] on molecular weights of salts dissolved in fused solvents confirms the earlier results of Foote and Levy. A large number of salts were used as solvents, including sodium, potassium, calcium, and barium chlorides, also sodium sulphate. Normal molecular weights were found.

Experiments by Rugheimer[26] on molecular weights of various chlorides dissolved in bismuth chloride gave results agreeing with those of Foote, that is, normal weights were found.

It is thus apparent that measurements of freezing point depressions in the case of salts dissolved in fused salts do not by any means confirm the belief that the solute in such cases is dissociated in the same sense that salts in water are; nor is there any relation between dissociation and conductivity in such cases. Indeed the results obtained remind one very much of what is very frequently observed with non-aqueous solvents at ordinary temperatures, and strengthen the conviction now gaining ground so rapidly, that aqueous solutions are altogether unique and exceptional. Whether or not we are justified in concluding, therefore, that equal uncertainty attaches to the dissociation of pure fused salts, that is those not dissolved in some other fused salt, is hard to decide. The most cogent evidence in favor of assuming dissociation in this case is the utter lack of any other hypothesis to replace it.

[24] Zeit. Phys. Chem. **78**, 550-72 (1912).
[25] Foote & Martin. Am. Chem. Jour. **41**, 451; Zeit. anorg. Chemie, **55**, 175.
[26] Ann. Chemie (Liebig) **339**, 297.

Although, as has been pointed out, the evidence tending to show that pure fused salts are dissociated is very weak when critically examined, the general belief of those working actively in this field is undoubtedly that dissociation does exist, and, in most cases at least, to a high degree. According to Lorenz,[27] a high degree of dissociation exists in solids as well as liquids, and the tremendous increase in conductivity often observed as the melting point is approached is due to the tremendous increase in ionic mobility. Conductivity in aqueous solutions, we believe, depends on two factors, the number of ions and their ionic mobility. The latter factor, it would appear, is the important one in the case of fused salts, very little change in the number of ions taking place as the temperature rises, but a great change occurring in the ionic mobility. The close proportionality existing between conductivity and fluidity is, of course, evidence in favor of this view, if we are willing to assume that ionic mobility and fluidity are proportional.

It must be emphasized again, however, that direct quantitative evidence showing the dissociation of pure fused salts has not been obtained as yet. Until such has been brought to light, the retention of the electrolytic dissociation theory for such cases can be regarded only as a temporary convenience.

[27] Lorenz, Vol. III, p. 290.

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CONDUCTION IN FUSED SALTS.

By H. M. Goodwin.

In considering the subject of conduction in fused electrolytes, it may be said at the outset that compared with the carefully-elaborated and well-verified theory of electrical conduction in aqueous solutions the present state of our knowledge is very incomplete. This is due in part to the experimental difficulties which are inherent in the accurate measurement at high temperatures, of properties whose large temperature coefficients demand the establishment and measurement of temperatures to within a few tenths of a degree. Until comparatively recently, data on such properties as the density, specific conductance and viscosity of fused salts, which were reliable to a few tenths of a per-cent, were not available, and even now much still remains to be accomplished in this field of research. Aside from experimental difficulties there are also theoretical difficulties presented by fused electrolytes which render conclusions regarding their constitution more difficult than in the case of aqueous solutions. These I shall endeavor to point out, and at the same time to indicate the conclusions which the data thus far accumulated seem to warrant us in drawing, in regard to the manner in which the current is probably conducted in molten salts. That conduction through fused inorganic salts is electrolytic in character, will not I think be seriously questioned by anyone at the present time. If we compare electrolysis of salts in a state of fusion and in aqueous solution, we find that the substances liberated at the electrodes are in many cases identical. Thus, for example, fused zinc chloride is decomposed into metallic zinc and chlorine gas, products which are identical with those resulting from the electrolysis of zinc chloride dissolved in water. Faraday, in his "Experimental Researches," included fused salts among the electrolytes studied and extended his law of electrolysis to include these.

Altho subsequent experiments inclined him to the view that under certain conditions a current might pass through an electrolyte without being accompanied by chemical decomposition, as required by his law, thus indicating that electrolytic conduction might be accompanied by something of the nature of metallic conduction, the extensive and careful experiments of Lorenz and his students at Zurich have shown that such anomalous results may be completely accounted for by secondary reactions, in virtue of which the products first liberated at the electrodes dissolve in the melt and subsequently diffuse and recombine. By taking proper precautions to eliminate these effects, Lorenz and Helfenstein were able to show, for example, that a current efficiency as high at 99.98 percent could be obtained in the case of fused lead chloride. From their experiments, we may regard Faraday's Law as having been experimentally verified for fusions, not in general to the degree of precision with which it has been shown to hold in the case of aqueous solutions, but to within the precision with which it has been possible to eliminate the effect of secondary reactions. Low current efficiency in a fusion electrolysis is far more likely to be due to a residual current resulting from the diffusion of the products of the electrolysis than to the presence of metallic conduction. So far as Faraday's Law is concerned, solutions and fusions may be considered in the same class and an ion of a given salt may, therefore, be assumed to carry the same electric charge whether the salt be fused or in solution. If electrical conduction is a convection phenomenon, of electrons in the case of metals and of ions in the case of electrolytes, we would naturally expect conduction in fused salts to depend upon factors which are analogous to those which determine conduction in solutions. In the latter case the conductivity is completely determined by the three following factors:

(a) The number of ions existing at any instant per unit volume, *i. e.*, to the concentration of the solute multiplied by the percentage of the time it is in the ionized condition.

(b) The velocity with which the respective ions migrate through the solution when acted upon by a given electric force.

(c) The quantity of electricity which is associated with and transported by each ion, *i. e.*, according to our present view, on

the number of uncompensated electrons attached to each anion and corresponding deficit of electrons in the case of the cations.

If we consider the conductance of one equivalent weight of salt dissolved in φ c. cm. of water the equivalent conductance Λ_φ is expressed by the well-known relation

$$\Lambda_\varphi = F\,\gamma\,(u_c + u_a)$$

If the same factors determine the magnitude of the conductance of an equivalent weight of the salt when it is in the fused state, the simplest hypothesis to assume is, that the equivalent conductance may be expressed by a formula similar to the above. Of the quantities in this equation, only two have been directly measured up to the present time, namely F and Λ_φ. The value of the former, the Faraday, is identical with the value in the case of solutions, namely 96,540 coulombs per gram equivalent. The experimental determination of the latter, the equivalent conductance, involves first the precise measurement of the specific conductance at accurately measured temperatures, and second correspondingly precise determinations of the specific volume of the salt at the same temperatures. Such measurements have been made the subject of several researches in recent years at Zurich, Charlottenburg and at the Institute of Technology, and the equivalent conductance of a number of salts is now known to within a few tenths of a percent.

TABLE I.

Salt	Temp. (t° Cent.)	Sp. Cond. Fused κ	Sp. Cond. n-Sol. at 18°	Eq. Cond. Λ at t°	Eq. Cond. $\Lambda\infty$ at 18°
$NaNO_3$	350	1.173	0.0660	52.87	105
KNO_3	350	0.673	0.0804	36.54	126
$AgNO_3$	350	1.245	0.0678	55.43	117
NaCl	850	3.50	0.0744	137.	110
KCl	850	2.30	0.0982	117.	131

In Table I are collected for comparison values of the specific and equivalent conductance of a few typical salts in the fused state and in aqueous solutions of normal and zero concentration (infinite dilution). It will be seen that whereas the specific

conductance of the salts is in all cases much greater in a state of fusion than in aqueous solutions, the converse is true with respect to their equivalent conductance, and this notwithstanding the much higher temperature of the fusion. Thus the conductance of one equivalent weight in grams of silver nitrate fused at 350° C., placed between electrodes 1 cm. apart, is 55.43 mhos, whereas the same quantity of the salt in a normal solution, *i. e.*, 1,000 c.c. of solution if poured between electrodes 1 cm. apart has a conductivity of 1,000 × 0.0678 = 67.8 mhos. In the latter case we know at any instant that $\gamma = \frac{\Lambda}{\Lambda_\infty} = \frac{67.8}{117} =$ 0.58, or 58 percent of the salt is in the ionized state, and that at 18° C. under a potential gradient of one volt per cm. the silver ions migrate towards the cathode with a velocity of about 1.7 cm. per hour, while the NO_3 ions migrate in the reverse direction with a velocity of 1.9 cm. per hour.

Now values of the equivalent conductance of the order of magnitude shown in column 5, Table I, may be accounted for either by a relatively high velocity of migration of comparatively few ions, by a low velocity of a large number of ions, or by intermediate values of each factor. Which of these assumptions corresponds to the facts? Unfortunately the methods which have led to a definite answer to these questions in the case of solutions are not applicable here, or at least with difficulty. For in a fusion of a pure salt transference experiments leading to Hittorf transport ratios are evidently impossible, and the determination of the ionization coefficient presents a problem of peculiar difficulty. Lorenz in an endeavor to determine the transport ratio of lead in lead chloride when dissolved in potassium chloride obtained evidence that migration occurs, in this case, however, the lead moving toward the anode as a constituent of a complex anion. This so far as I know is the only attempt which has been made to carry out transference experiments in fused salts. Direct measurements of the velocity of migration of the ions in fused salts by the moving boundary method have, it is true, been attempted, but the experimental difficulties arising from convection and diffusion phenomena at high temperatures have rendered these measurements thus far of uncertain value. This problem is being worked upon at the present time in our electro-

chemical laboratory, but until such measurements have been carried to a definite issue, conclusions regarding the degree of ionization of fused salts must rest on indirect evidence. At present such evidence is based upon three distinct types of data:

First, a comparative study of the effect of temperature on their conductivity and fluidity.

Second, the effect of one salt on the melting point of another.

Third, electromotive force measurements of cells composed of fused electrolytes.

TABLE II.

Comparison of Conductivity and Fluidity of Potassium Nitrate.

Temperature	F	$10^4 \frac{\kappa}{F}$	Molal Fluidity, $f = F/\phi$	$\frac{\Lambda}{f}$
340	36.1	178	0.666	52.3
350	38.0	177	0.698	52.3
360	40.1	175	0.736	52.2
370	42.3	174	0.775	51.7
380	44.5	172	0.810	52.2
390	46.7	170	0.845	51.9
400	48.8	169	0.880	51.9
410	51.1	167	0.923	51.6
420	53.3	166	0.959	51.6
430	55.6	165	0.989	51.9
440	57.9	163	1.022	51.9
450	60.2	162	1.062	51.9
460	62.5	160	1.100	51.6
470	64.8	159	1.139	51.6
480	67.1	157	1.174	51.7
490	69.4	156	1.207	51.5
500	71.8	155	1.243	51.4

F = ordinary fluidity = reciprocal of viscosity.
f = molal fluidity = reciprocal of viscosity $\times$ molecular volume.
κ = specific conductance.
Λ = equivalent conductance.

The first to investigate the relation between the specific conductance and viscosity of fused salts was Foussereau, who in 1888 published measurements of these properties for sodium and potassium nitrate over a considerable range of temperature. He concluded that the product of the two properties was a constant independent of the temperature. The problem has more recently been taken up by Lorenz, Arndt and myself in conjunction with Kalmus and Mailey. Our results lead to the conclusion

that Foussereau's law is only approximately true. They indicate, however, in the case of certain salts that the equivalent conductance of a fused salt increases with the temperature at the same rate as the fluidity of a corresponding equivalent weight of the salt in question, while for others the equivalent fluidity increases slightly more rapidly than the equivalent conductance; in other words the ratio $\frac{\Lambda}{f} = \frac{\text{equivalent conductance}}{\text{equivalent fluidity}}$ is either a constant or decreases slowly with increasing temperature. Thus proportionality was found to hold within the experimental error for a range of temperature of over 100° for KNO_3 as shown in Table II. In the case of $NaNO_3$ $LiNO_3$, $AgNO_3$, $PbCl_2$, $PbBr_2$-$K_2Cr_2O_7$, the ratio $\frac{\Lambda}{f}$ decreased several percent for a rise of temperature of 100°, an amount greater than could be attributed to experimental error. The results obtained with silver nitrate shown in Table III illustrate the magnitude of the change.

TABLE III.

Comparison of Conductivity and Fluidity of Silver Nitrate.

Temperature	F	$10^4 \frac{\kappa}{F}$	Molal Fluidity, $f = F/\phi$	$\frac{\Lambda}{f}$
230	24.0	308	0.557	57.2
240	25.8	305	0.598	56.7
250	27.7	301	0.642	56.3
260	29.5	298	0.681	56.3
270	31.3	295	0.720	55.8
280	33.1	292	0.760	55.5
290	34.9	289	0.798	55.5
300	36.7	286	0.836	55.3
310	38.5	283	0.873	54.8
320	40.2	280	0.911	54.7
330	42.0	277	0.952	54.3
340	43.8	275	0.988	54.3
350	45.5	273	1.022	54.3

F = fluidity = reciprocal of vicosity.
f = molal fluidity = reciprocal of viscosity × molecular volume.
κ = specific conductance.
Λ = equivalent conductance.

Now it seems probable that the velocity with which an ion migrates at different temperatures is proportional to the fluidity

of the medium through which it moves, provided the composition of the ion and constitution of the medium do not change appreciably with the temperature. For dilute solutions in which the ionization is constant Walden has shown this conclusion to be verified in a large number of cases. If proportionality between the properties of migration velocity and fluidity be assumed to hold for such salts as potassium nitrate, in which the ratio of equivalent conductance to fluidity is constant, the increase in conductivity with temperature may be wholly accounted for by an increase in migration velocity; hence it would follow that

TABLE IV.

Equivalent Conductance of 5 Mols KNO_3 + 5 Mols $NaNO_3$.

Temperature	Specific Conductance, κ	Density, D	Equivalent Conductance	Equivalent Conductance Computed	Difference
220	0.3300	1.967	13.64		
300	0.6630	1.907	32.23		
310	0.7043	1.899	34.54		
320	0.7475	1.892	36.80		
330	0.7890	1.884	39.01		
340	0.8293	1.876	41.17	42.63	—1.46
350	0.8680	1.869	43.25	44.71	—1.46
360	0.9050	1.862	45.27	46.76	—1.49
370	0.9410	1.854	47.27	48.88	—1.61
380	0.9768	1.847	49.26	50.78	—1.52
390	1.011	1.839	51.20	52.74	—1.54
400	1.045	1.832	53.13	54.67	—1.54
410	1.078	1.824	55.05	56.61	—1.56
420	1.111	1.817	56.95	58.50	—1.65
430	1.143	1.809	58.85	60.38	—1.53
440	1.174	1.802	60.68	62.25	—1.57
450	1.205	1.794	62.56	64.09	—1.53

the ionization of such a salt remains unchanged. The rapid increase in conductivity of a salt as it passes through its melting point (an isothermal phenomenon) is sufficient proof that temperature is not primarily the cause of the high conductivity of the molten mass. Those cases in which Λ increases less rapidly than f may be explained on the assumption that the ionization coefficient decreases slightly with rising temperature. Noyes has proved that this does occur in the case of a number of inorganic salts in aqueous solution, when heated to high temperature. Thus sodium chloride in normal solution is ionized 83

percent at 18° and only 60 percent at 306°. Substances which become less ionized the higher the temperature dissociate with an evolution of heat, and this property is characteristic of substances which are normally *highly ionized,* such as HCl, NaCl, etc. Substances like water, which are but slightly ionized, dissociate with absorption of heat and have a positive temperature coefficient of ionization. On the hypothesis that fluidity and migration velocity are proportional, present experimental evidence indicates that the ionization of fused salts varies but little with rising temperature and tends to decrease rather than increase. As this is known to be a characteristic of highly ion-

TABLE V.

Fluidity of 5 *Mols* KNO_3 + 5 *Mols* $NaNO_3$.

Temperature	F	$10^4 \frac{\kappa}{F}$	Molal Fluidity, $f = F/\phi$	$\frac{\Lambda}{f}$	Molal Fluidity, f' Computed	$f - f'$
340	41.1	196	0.826	49.7	0.783	0.043
350	43.5	199	0.875	49.4	0.822	0.053
360	45.7	198	0.916	49.5	0.860	0.056
370	48.0	196	0.949	49.7	0.900	0.049
380	50.3	194	1.000	49.3	0.945	0.055
390	52.6	192	1.039	50.6	0.987	0.052
400	54.8	191	1.075	49.7	1.030	0.045
410	57.2	189	1.124	48.7	1.076	0.048
420	59.4	187	1.160	49.2	1.119	0.041
430	61.7	185	1.200	49.2	1.149	0.051
440	64.0	183	1.238	49.0	1.191	0.047
450	66.3	181	1.277	49.1	1.231	0.046

ized salts, a high rather than a low degree of ionization is indicated. This conclusion is further borne out by the results obtained with mixtures. Thus the equivalent conductance of an equi-molecular mixture of sodium and potassium nitrates is less than that computed additively from the two components, *i. e.,* the mixture conducts less well than it would if the ionization of both salts remained unchanged. This is shown by the figures given in Table IV. The fluidity of the mixture on the other hand is greater than that of either component at the same temperature. Yet the ratio of these two properties is constant within the error of experiment from 340° to 450° as seen in Table V.

An experiment of Arndt's is also interesting in this connection. He found from measurements at 900° C. of the conductivity and viscosity of solutions of sodium meta-phosphate in boracic anhydride, varying in concentration from 100 percent to 0.5 percent, that the product of the equivalent conductance and viscosity was practically constant for all concentrations, from which he concluded that the former salt must be practically completely ionized in the fused state under the above conditions. At temperatures below 900° the relations are, however, less simple of explanation.

The above conception of the constitution of fused electrolytes is further strengthened by experiments of quite a different

TABLE VI.

Salt	Melting Point	M = Molecular Weight	L = Latent Heat of Fusion	$\gamma = ML$ = Molecular Heat	Cs = Specific Heat Sclid	MCs = Molecular Heat Solid	Cl = Specific Heat Liquid
KNO_3	308	101	25.5	2,570	0.292	29.5	0.333
$NaNO_3$	333	85	45.3	3,690	0.388	33.0	0.430
$LiNO_3$	250	69	88.5	6,100	0.387	26.7	0.390
$AgNO_3$	218	170	15.2	2,580	0.195	33.2	0.195
AgCl	455	143	21.3	3,050	0.100	14.3	0.129
TlCl	427	240	16.6	3,980	0.0580	13.9	0.0590
$PbCl_2$	498	278	18.5	5,150	0.0778	21.6	0.121
AgBr	430	188	12.6	2,370	0.0755	14.2	0.0760
TlBr	460	284	12.7	3,610	0.0525	14.6	0.0800
$PbBr_2$	488	367	9.9	3,650	0.0566	20.8	0.0780
$NaClO_3$	255	106	49.6	5,250	0.320	32.4	0.325
$K_2Cr_2O_7$	397	295	29.8	8,800	0.231	68.3	0.335

character. In 1909, I carried out in collaboration with Dr. Kalmus an investigation of the specific heats of a number of inorganic salts melting below 600° C., in the solid and in the liquid state, together with their latent heats of fusion. The results are shown in Table VI; in all cases the specific heat C_1 in the liquid state is seen to be greater, but in most cases only slightly greater than the specific heat C_s in the solid state, while the latent heat of fusion is small compared, for example, with that of ice (80 cal.). Lithium nitrate seems to form the one exception. In other words, comparatively little energy is required to cause the solid salt to pass over into the liquid state at its melting point, and

the heat capacity of the substance in the two states is not widely different. This indicates that the molecular condition of the salt is not widely different in the two states.

In passing through the melting point there is therefore no indication of an energy change sufficient to produce a sudden ionization of the salt and thus explain the enormous increase in electrical conductivity accompanying the change of state. The values of the molecular heat of fusion are in fact less than the heat required to melt many non-electrolytic (organic) compounds. The energy absorbed is sufficient, however, to so weaken the forces of cohesion between the molecules and ions that a sufficient fluidity results to permit free migration of any already existing ions as soon as an electromotive force is applied.

Moreover, from a knowledge of the latent heat of fusion L, and absolute melting point T, of a solvent, the lowering of its melting point produced by the addition of a second substance can be calculated by van't Hoff's well-known formula.

$$\Delta T = \frac{RT^2}{M_o L_o}, \frac{N}{N_o}.$$

If a substance like sodium chlorate is used as a solvent and other salts containing either sodium or the chlorate group be added in not too large quantities, the depression of the freezing point should be "normal," that is, proportional to the total amount of dissolved salt provided the active mass of the sodium or chlorate ion of the solvent is large compared with that of the solute, which would be the case if the solvent is in a high state of ionization. This has been demonstrated by both Stortenbecker and Lewis. On the other hand, if a salt like potassium nitrate be added, both of whose ions are different from those of the solvent, the depression of the freezing point should be twice as great as in the corresponding case of a sodium salt or chlorate. The results of Foote and Levy, 1907, confirm both of these consequences of theory. Similar data by Plato (1906) and Kalmus (1909) find a satisfactory explanation on the assumption of a high degree of ionization of the solvent. But here again insufficient data prevent the calculation of its exact value.

Finally experiments on the electromotive force of cells in which

the electrolyte is composed of a fused salt have been carried out first by Richards and Gordon at Harvard and later by Lorenz and his students at Zurich, and also in our laboratory; these all point to a state of high ionization in a fused salt. Consider for example the e. m. f. of a concentration cell of the type

$$\text{Ag} \;\Big|\; \begin{matrix}\text{AgNO}_3 \text{ in } \text{NaNO}_3 \\ \text{Conc.} = C_1.\end{matrix} \;\Big|\; \begin{matrix}\text{AgNO}_3 \text{ in } \text{NaNO}_3 \\ \text{Conc.} = C_2.\end{matrix} \;\Big|\; \text{Ag}$$

If the liquid junction potential be neglected, and Nernst's osmotic theory of the cell be applied to the combination, the e. m. f. should be expressed by the formula

$$e = \frac{RT}{F} \; ln. \; \frac{Ag_1}{Ag_2},$$

TABLE VII.

$AgNO_3$ in $NaNO_3$.

Equivalent Concentration of $AgNO_3$ at 400° C.		Temp.	E (Observed)	$E=\frac{RT}{F} ln \frac{c_1}{c_2}$	Δ Difference
c_1	c_2				
0.00986	0.06206	350	—0.1014	—0.0986	+0.0028
0.00986	0.06206	350	—0.0996	—0.0986	+0.0010
0.00986	0.1220	337	—0.1335	—0.1320	+0.0015
0.06206	0.1220	349	—0.0370	—0.0362	+0.0008
0.5565	0.1220	340	+0.0781	+0.0800	—0.0019
0.5565	0.00986	340	+0.2094	+0.2130	—0.0036
0.5250	0.04999	329	+0.1230	+0.1220	+0.0010

where $\frac{Ag_1}{Ag_2}$ is the ratio of the silver-ion concentration at the two electrodes respectively. Now it can be shown if the solvent $NaNO_3$ is highly ionized into Na and NO_3 ions that this ratio $\frac{Ag_1}{Ag_2}$ is equal to the ratio $\frac{c_1}{c_2}$ of the total concentration of the dissolved $AgNO_3$ at the two electrodes respectively, so long as the number of NO_3 ions contributed by the solute is relatively small compared with the number of similar ions in the solvent. Table VII contains data obtained by Wentworth and myself which show that these conditions are fulfilled in solutions the concentrations of which are not much over half normal. When the percent of

silver nitrate is increased beyond this amount, up to 100 percent, the proportionality $\frac{Ag_1}{Ag_2} = \frac{c_1}{c_2}$ no longer holds, as shown by the data in Table VIII. Thus the ratio $\frac{Ag_1}{Ag_2}$ calculated from the measured e. m. f. for pure $AgNO_3$ *vs.* 0.01-normal solution in $NaNO_3$, is only one half that corresponding to the total concentration ratio. Replacing $AgNO_3$ by $AgClO_3$ as solute, the above conditions should no longer apply, and this we found to

TABLE VIII.

Ag	*$AgNO_3$ in $NaNo_3$ Conc. = c_1*	*$AgNo_3$ in $NaNo_3$ Conc. = c_2 = 0 01 normal*	*Ag*

Equivalent Concentration of $AgNO_3$, c_1	$E = \frac{RT}{F} ln \frac{c_1}{0.01}$	$\frac{c_1}{0.01}$	$\frac{(Ag)_1}{(Ag)_{.01}}$ Computed from Formula
0.531	0.2105	53	55
0.531	0.2068	53	53
1.065	0.2412	107	100
1.780	0.2670	178	159
2.345	0.2810	235	199
4.63	0.3071	463	331
7.38	0.3279	738	528
13.20	0.3505	1320	764
22.48*	0.3720	2250	1100

*Pure $AgNO_3$

be verified by experiment. On the basis of data similar to the above, Richards and Gordon, and Lorenz have computed the ionization of pure fused $AgNO_3$ to be 58 percent at 236° and of pure fused AgCl to be 60 percent at 730° respectively. The assumptions involved in these calculations, however, are so questionable that I believe little reliance can be placed upon these figures as representing actual facts. Lorenz himself admits that he regards them only as first estimates. A method of computing the degree of ionization of a fusion suggested in 1899 by the late Professor Abegg, based on the assumption that the decomposition potential of an ion is independent of the medium from which it is liberated, has led as yet to no definite results. As the evidence for electrolytic conduction in solids is to be discussed by others, I have not touched upon this phase of the subject, altho it is intimately connected with the present one.

In conclusion we may say that, from the experimental evidence which we now possess, electrical conduction in fused electrolytes is a convection phenomenon not unlike that which takes place in solutions, the electrolyte being in a high state of ionization. The actual velocity with which the ions move, their relative velocity, as well as their number per unit volume, persent problems important from the technical as well as from the theoretical side, which still await solution.

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A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE ELECTRICAL PROPERTIES OF SOLUTIONS OF METALS IN AN ELECTROLYTIC SOLVENT.

By Charles A. Kraus.

I had intended to discuss certain investigations which are of particular interest in relation to the conduction process, since they are concerned with a system which, so to speak, forms a connecting link between electrolytic and metallic conductors. These investigations furnish evidence as to the fundamental assumption that the current in metals is carried by charged carriers, and, in particular, that it is the negative carrier which is chiefly concerned in this process.

However, I shall not task your patience with a discussion of all the investigations involved. I shall merely describe a single set of experiments which will show how electrolytic and metallic conductance are related. In this connection it is to be borne in mind that metallic conduction is characterized by an absence of material effects accompanying the passage of a current.

If we examine a solution of a metal, as, for example, of sodium, in liquid ammonia,[1] we find that it conducts extremely well. I have determined the relation between the equivalent conductance of the metal and its concentration over a large range of concentrations. At extremely high dilutions the equivalent conductance approaches very near to a limit whose value is 1026 (expressed in the customary units). As the concentration of the metal increases, its equivalent conductance decreases, the conductance-concentration curve obeying the law of mass action for the dissociation of a binary electrolyte. At higher concentrations the curve changes its form and, in the neighborhood of 0.05 normal, the conductance reaches a minimum value of 474 units, after which it again increases, the rate of increase being the greater the greater the concentration of the solution. In the neighborhood of normal concentration the eqivalent conductance

[1] The details relating to the results described in the present address will appear in forthcoming papers. Many other properties of these solutions have already been described elsewhere; J. Am. Chem. Soc.; **29**, 155 (1907); **30**, 653, 1197, 1323 (1908).

is 6000, and at twice normal concentration it reaches the enormous value of 100,000.

By way of comparison, I may state that at infinite dilution in liquid ammonia, sodium salts have an equivalent conductance of about 300, to which value the sodium ion contributes 130 units. I have been able to show that the conductance of the solution of metallic sodium is due to charged carriers, the positive carrier being identical with the sodium ion of common sodium salts. The negative ions in solutions of metallic sodium and potassium are identical. In dilute solutions the negative ion of the metal moves seven times as fast as the sodium ion. I have been able to show by independent means that as the concentration of the metal increases, the velocity of the negative carrier increases. In a normal solution the speed of the negative carrier is several hundred times that of the sodium ion. This explains the peculiar form of the conductance-concentration curve. Although the number of carriers is decreasing with increasing concentration, the speed of the negative carriers increases at such a rate as to overbalance the effects due to decrease in their number, and finally the form of the curve is almost entirely due to the change in the speed of the negative carriers. In a solution containing one atom of sodium to five molecules of ammonia, the specific conductance has reached a value one-half that of metallic mercury. These solutions behave like metals in respect to all their physical properties.

From what I have said it will be plain that the solutions of sodium form a connecting link between metallic conductors on one hand and electrolytic conductors on the other, and we are able to pass continuously from one to the other. In dilute solutions the negative carrier is surrounded by an envelope of solvent molecules which reduces its speed to such an extent that a considerable portion of the current is carried by the positive ion. As the concentration of the solution increases, the negative carrier is, at times, free of its envelope, which results in an increase in the mean speed of the negative carrier and a corresponding increase in the conductance of the solution. When the concentration reaches a sufficiently high value, an appreciable fraction of the negative carriers will be free of their envelopes at any given instant of time, the amount of current carried by the solvated negative carriers, as well as by the positive carriers, becomes inappreciable, and the conduction process is essentially metallic in character.

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE HALOGEN HYDRIDES AS CONDUCTING SOLVENTS.

By D. McIntosh.

The investigation of the conductance of certain substances in the liquefied halogen hydrides has shown clearly some sharp distinctions between non-aqueous and aqueous solutions. Since these results have been published[1] it is unnecessary to describe the anomalies in detail; and as solutions of the halogen hydrides in general exhibit the same characteristics it will suffice to discuss only one solvent—hydrogen bromide.

Hydrogen bromide is a colorless liquid, boiling at — 66° C. and freezing at — 86° C. Its density at the boiling point is 2.16, and the heat of vaporization is 17.5×10^{10} ergs (417 calories) for each gram molecule. It consists almost entirely of single molecules, the variation of surface energy with temperature being 2.03 ergs per degree. Its viscosity is lessened about 0.6 percent for each degree rise in temperature from its freezing point. When pure it is a very poor conductor of electricity, a centimeter cube having a conductance of 0.008×10^{-6}, that of the purest water being 0.04×10^{-6}.

Hydrobromic acid is almost without solvent action on inorganic compounds. Many organic substances, however, such as the hydrocarbons, ethers, alcohols, esters, etc., dissolve readily in it, and those containing oxygen or nitrogen atoms invariably yield conducting solutions.

These solutions show the peculiarity that with increasing dilution the molecular conduction decreases. Fig. I, shows clearly the distinction in conduction between aqueous and the halogen-hydride solutions. At high dilutions, as Archibald has pointed out, the molecular conductance does not decrease but may even increase slightly with dilution.

[1] Steele, McIntosh and Archibald, Trans. Royal Society **205**, 99 (1903).

(1) Substances dissolved in halogen hydrides;

(2) Potassium chloride in water;

(3) Sodium carbonate in water;

(4) A solution of ammonia in water.

The anomalous behaviour of these as compared with aqueous solutions would disappear if we could regard the organic body as the solvent and the halogen hydride as the solute. But this can not be done for the following reasons.

(1) On cooling, crystals of the pure acid separate out.

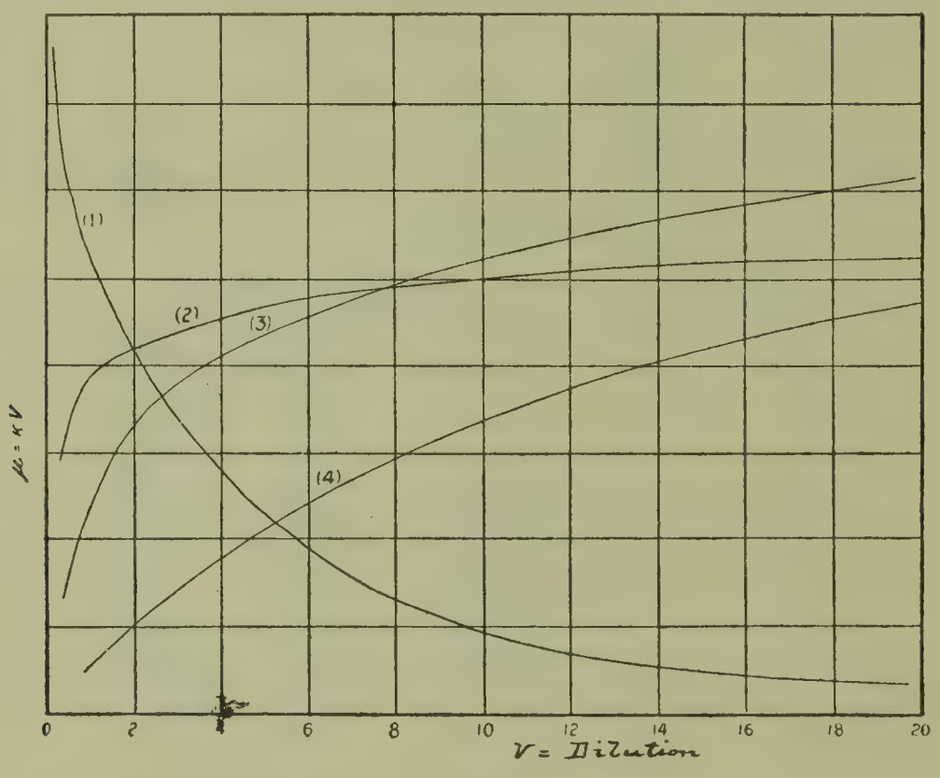

FIG. 1.

(2) Solid substances such as ethylamine hydrobromide, urea, etc., dissolve and give conducting solutions of the same type as those of the ethers, alcohols, etc. To regard a solid as solvent is contrary to the ordinary conception of the rôle of the dissolving medium.

(3) Organic bodies containing oxygen form definite compounds with the acids, evolving large amounts of heat. Many of these compounds have been isolated and their properties determined. They dissolve in either the organic constituent or the halogen hydrides, but in the latter case conduct much better and exhibit the anomalous behaviour previously mentioned.

Here the halogen hydride is apparently the solvent of these compounds.

(4) Finally Steele has determined the migration ratios in these solutions. He found that Faraday's law is exactly obeyed; *i. e.*, the hydrogen liberated at the cathode during electrolysis is exactly that calculated from the silver deposited in a silver coulometer, while the organic body increases in concentration at the cathode. This increase can be brought about in two ways: by the migration of the organic substance to the cathode, or by the hydrobromic acid being transferred to the anode. On the former assumption, 96,500 coulombs move but a fraction of a gram molecule; on the latter 15-20 gram molecules of hydrobromic acid must be transferred. We conclude, therefore, that the halogen hydride is the solvent in solutions containing only a small percentage of organic bodies.

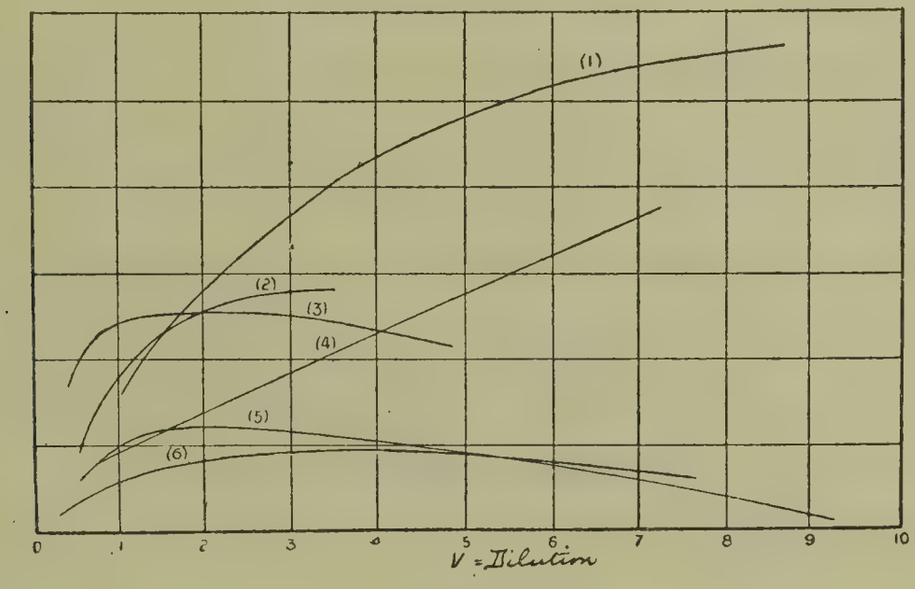

FIG. 2.

(1) Triethylammonium chloride in hydrogen iodide.
(2) Nicotine in hydrogen sulphide.
(3) Ether in hydrogen iodide.
(4) Triethylammonium chloride in hydrogen sulphide.
(5) Ethyl benzoate in hydrogen iodide.
(6) Acetone in hydrogen bromide.

The compounds formed in solution may be quite complex. With ethyl acetate and hydrogen bromide we have obtained three definite compounds. With this acid ether gives two, $C_4H_{10}O.HBr$ and $C_4H_{10}O.2HBr$, the latter crystallizing out when a large excess of acid is present. Even more complicated salts

may exist in solution and may yield many complex ions. The molecular weights of these compounds have not been determined with any degree of accuracy. The values obtained seem to point to association in dilute solutions, and dissociation in the more concentrated solutions; while the variations in the migration ratios show, as might be expected, the opposite tendency.

In order to explain the anomalies in terms of the dissociation theory we may assume that compounds of the type $(C_4H_{10}O)_m$ (H Br) are formed, and that these dissociate and conduct the electric current. If K be the specific conductance and V the dilution, it may be shown that $K\ V^n$ is constant, where the dissociation is complete. If the dissociation increases with dilution, $K\ V^n$ should vary with dilution in the same way as the molecular conductivity for water solutions. This point is brought out in Fig. 2 where $n = 2$ or 3.

Conclusions.

Organic substances undoubtedly give compounds with the halogen hydrides which conduct the current, and the variation of molecular conductance with concentration is in the opposite direction to the variation in aqueous solution. By assuming the existence of more complex compounds than those isolated we can explain this behaviour and bring our results into agreement with the ionic theory. Whether such assumptions are justifiable or not can be settled by exact molecular weight determinations, which we are, at present, endeavoring to make.

McGill University,
Montreal, March 29, 1912.

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE ELECTRICAL CONDUCTANCE OF CONCENTRATED AQUEOUS SOLUTIONS OF ELECTROLYTES.

By Edward W. Washburn.

In the case of dilute aqueous solutions of electrolytes we have in the Ionic Theory a set of general laws which correlate to a remarkably complete degree the greater part of our knowledge concerning such solutions and, although there are several important questions still awaiting their final interpretation in terms of this theory, on the whole our theoretical knowledge of dilute solutions has now reached such an advanced stage as to warrant the expectation that the data obtained by a systematic study of more concentrated solutions will enable us to extend considerably the present boundaries of our quantitative theoretical knowledge concerning solutions of electrolytes. It may, therefore, not be without interest to examine briefly the nature of some of the problems which confront us when we attempt to go from the comparatively simple conditions which prevail in dilute solutions to the much more complicated ones which we encounter in concentrated solutions, and it is with this purpose only, that I venture to comply with President Whitney's request and present a paper upon a subject concerning which there is so little real knowledge at the present time.

(I.) Distinction Between "Dilute" and "Concentrated" Solutions.

Although there is no sharp line between "dilute" solutions and "concentrated" ones, it is possible to make a practical distinction between them, and the following is offered as a satisfactory working definition of a "dilute" solution. A dilute solution is one is which the mole-fraction of the solute is small and in which further dilution produces only a negligible change in the "nature of the medium" as regards some specific property. The term "nature of the medium" includes a number of factors, and a

solution may be at the same time either "dilute" or "concentrated" according to which factor or factors of the nature of the medium are under consideration. For example, the viscosity of a ¼ normal potassium chloride solution at 25° is not altered more than about 0.1 percent by further dilution. For this degree of accuracy, therefore, all potassium chloride solutions at 25° and of any concentration up to ¼ normal might be classed as "dilute" solutions with respect to those properties which are determined by the viscosity of the medium. If, however, we consider the influence of the nature of the medium upon the osmotic pressures[1] of the potassium and chloride ions we must place our concentration limit much lower, at about 0.01 normal in fact. That is, up to this concentration the "nature of the medium" does not change sufficiently to produce more than a one percent change in the osmotic pressures of the ions. For the un-ionized molecules it appears at present that a similar statement could not be made unless the concentration limit were placed at about 0.0005 normal.

That factor of the "nature of the medium" which influences the osmotic pressure of a given molecular species in a solution may be called the thermodynamic environment of the species in question, and the osmotic pressure of any molecular species in any solution may be conveniently considered as determined by two factors; (*a*) the mole-fraction of the constituent and (*b*) its thermodynamic environment. The second of these factors will in general, for a solution of two components, be a function of the first, but in the two limiting cases of a "dilute solution" and an "ideal solution," the thermodynamic environment is constant and independent of the relative amounts (*i. e.*, the mole-fractions) of the different molecular species which make up the solution. For these two limiting cases the general laws governing the solution are comparatively complete and well understood at the present time, and the problem of the future is, therefore, primarily a problem of solutions in which the thermodynamic environment changes with the concentration and not merely a problem of solutions in which the mole-fraction of the solute is large. It is in the former sense that I shall employ the term "concentrated solutions."

[1] Or the "thermodynamic potentials" or the "fugacities."

(II.) The Factors Which Determine the Conductance of a Concentrated Aqueous Solution of an Electrolyte.

Imagine one equivalent weight in grams of a chemically pure fused salt, such as silver nitrate, placed between two parallel electrodes one centimeter apart and of indefinite area. The conductance of this liquid between the two electrodes is the equivalent conductance of the salt. If now we add water gradually and measure the conductances of the solutions thus obtained we will be able to construct the entire equivalent conductance curve for the salt, from an infinitely concentrated solution (*i. e.,* the pure fused salt) to an infinitely dilute solution. So far as I am aware, this has not as yet been done for any salt, although it would be quite possible to carry out such measurements in the case of silver nitrate and water at any temperature above 209°. In a number of instances, however, both with aqueous and non-aqueous solutions, the equivalent conductance curve has been traced back from the pure solvent to solutions of high concentrations. Among the solutions which have been invstigated in this way, the following may be mentioned: sodium hydroxide in water;[2] potassium iodide in liquid iodine;[3] organic acids in the liquid hydrogen halides;[4] solutions in liquid methylamine;[5] solutions of potassium iodide in water;[6] solutions of amines in acetic and propionic acids;[7] and solutions of salts in liquid sulphur dioxide.[8]

The general forms of the curves obtained in most of the cases cited have been shown by the different investigators[9] to be entirely explicable by the variation in the viscosity of the medium and in its dissociating power. In a few instances, notably the solutions studied by Steele, McIntosh and Archibald and those studied by Sakhanov, the chief determining factor seemed to be the presence of a compound between solute and solvent whose complexity changed very markedly with change in composition or in

[2] Bousfield and Lowry, Phil. Trans. (A) **204**, 289 (1903).

[3] Lewis and Wheeler, Proc. Amer. Acad., **41**, 419 (1906).

[4] Steele, McIntosh and Archibald, Phil. Trans. (A) **205**, 99 (1903); and Archibald, J. Amer. Chem. Soc., **29**, 1416 (1907). See also, *Ibid,* **34**, 584 (1912).

[5] Franklin and Gibbs, J. Amer. Chem. Soc., **29**, 1389 (1907).

[6] Sloan, J. Amer. Chem. Soc., **32**, 946 (1910).

[7] Sakhanov, J. Russ. Phys. Chem. Soc., **43**, 534 (1911).

[8] Franklin, J. Phys. Chem., **15**, 675 (1911).

[9] See especially Franklin's (l.c.) discussion of the general types of curves.

temperature. At all events we can say that all of the equivalent conductance curves thus far obtained are entirely explicable, qualitatively at least, on the basis of variations in the physical properties of the medium and in the nature of the ions which conduct the current; and, however hypothetical these explanations may at present appear in individual cases, they are certainly not unreasonable ones and they indicate pretty clearly the nature of the factors which must be considered if we are to obtain a quantitative interpretation of the conductivity of concentrated solutions.

It has seemed to me that this problem could be most readily attacked in the case of aqueous solutions of strong electrolytes by the study first of solutions of salts of the uni-univalent type in the concentration interval between 0.1 and 1.0 normal, that is, by the gradual extension of our present limits, taking up first those factors whose influence is first apparent as we go beyond the region of what we usually regard as dilute solutions. Using KCl as a typical salt of this type we may analyze our problem into the following factors:

1. The change in the number of the ions owing to the *increase in the quantity of the salt.*

2. The change in the number of the ions owing to the change in the *ionizing power of the medium.*

3. The decrease in the conductance owing to the increase in the *viscosity of the medium* through which the ions are moving.

4. The decrease in the *degree of hydration* of the ions and a consequent increase in their mobilities.

5. The possible formation of complex ions of the type $[(KCl)_x K]^+$ and $[(KCl)_y Cl]^-$, producing a decrease in the conductance.

6. An increase in conductance owing to a *Grotthus-Chain action,* thus practically reducing the distance which an ion must move between the electrodes.

7. Increasing quantities of *hydrogen and hydroxyl ions,* due to an increased degree of ionization of the water.

The determination of the degree of ionization of the salt will give us a quantitative measure of the influence of the first two factors which are the ones having the greatest effect upon the conductivity of the solution. The discovery of a satisfactory

method for determining the degree of ionization in the concentrated solutions is therefore the first requisite to further progress in this direction. As pointed out elsewhere,[10] the methods which depend upon the measurement of the freezing point, vapor pressure or related quantities cannot be employed for this purpose, at any rate not in the present state of our knowledge. Our only resource is, therefore, to make use of the conductivity itself, and in doing this the first and most important factor which must be taken into account is the effect of the viscosity of the medium upon the mobilities of the ions, as this is probably the factor whose influence is first apparent as we go beyond the region of dilute solutions.

(III.) The Viscosity Factor.[11]

The calculation of the degree of ionization by means of the relation: $\gamma = \frac{\Lambda}{{}_0\Lambda}$, is based upon the assumption that the ions experience the same resistance in moving through the solution as they do through pure water. This assumption is justified if the solution be sufficiently dilute, but if an accuracy of a few tenths of one percent is aimed at, the term *sufficiently dilute* must be generally interpreted as signifying not greater than 0.01 molal, and even here the error introduced by this assumption may amount to nearly one percent in the case of some uni-univalent salts. The following table shows the magnitude of this effect in 0.1 molal solutions for some extreme cases.

TABLE I.

Relative Viscosities of Some 0.1 Molal Aqueous Solutions.

Salt	t	η/η_0
$CsNO_3$	0	0.98
$LiIO_3$	18	1.03
NaOH	18	1.025
Na_2HPO_4	18	1.07
NaH_2PO_4	18	1.03
Na_3PO_4	18	1.08
Na benzoate	25	1.05
Na hydrocinnamate	25	1.07
Na isovalerate	25	1.06

[10] J. Amer. Chem. Soc., 33, 1461 (1911).

[11] A more detailed discussion of the influence of this factor and the methods of correcting for it is given in J. Amer. Chem. Soc., 33, 1463 (1911).

If the ions were spheres, large in comparison with the molecules of the medium through which they were moving, their velocities would by Stokes' law be proportional to the first power of the fluidity of the medium, or

$$\Lambda_I = kf \tag{1}$$

where Λ_I is the equivalent conductance of the ion and f the fluidity of the medium. This assumption leads to the following equation for the degree of ionization of a salt in a solution whose relative viscosity is η/η_0.

$$\gamma = \frac{\Lambda\eta}{\Lambda_0\eta_0} \tag{2}$$

This equation has been employed by a number of investigators[12] and is undoubtedly an improvement over the one which neglects entirely the viscosity influence. The chief objection to it is that the ions are not spheres, large in comparison with the molecules of the water, and hence strict proportionality between ionic mobility and fluidity is not to be expected. In fact it has been shown theoretically by Cunningham[13] and experimentally by Millikan[14] that even in the case of perfect spheres Stokes' law breaks down when the spheres become comparable in size with the molecules of the medium through which they are moving, and the modification of the law derived by Cunningham to correct for this deviation has been confirmed by the experiments of Millikan. In the case of electrolytic ions not only is their size of the same order of magnitude as that of the water molecules, but they may deviate considerably from a spherical shape owing either to hydration, in the case of single-atom ions, or to the atomic grouping in the case of radicals. As the magnitude of the deviation from the spherical shape cannot be calculated and allowed for, it will be necessary to proceed empirically.

In view of the uncertainty regarding the magnitudes of some of the other factors in our problem (as will be explained further below) we would not at present be justified, in the case of the viscosity factor, in employing an empirical relation containing

[12] *e. g.* Bousfield and Lowry, *loc. cit.*

[13] Cunningham, Proc. Roy. Soc. Lon. (*A*) **83**, 357 (1910).

[14] Millikan, Phys. Rev., **32**, 349 (1911).

more than two constants. Proceeding on this basis, therefore, the simplest modification of equation (1) which suggests itself is the introduction of an empirical constant, m, as the exponent of the fluidity in place of unity which is required by Stokes' law, thus giving us,

$$\Lambda_I = k_I f^{m_I} \qquad (3)$$

This constant, the "fluidity exponent," would vary with the nature of the ion, its size, shape and surface, and possibly to some extent also with the nature of the molecules composing the medium through which the ion is moving; but since these factors may be regarded as secondary ones which operate simply to produce deviations from Stokes' law, we might expect that the fluidity exponents would not vary very greatly from unity in the case of the different ions.

There are several ways in which this relation may be tested. The most obvious one is to determine the ionic conductances in media of different fluidities. In the case of aqueous solutions the variation in the fluidity can be brought about by (*a*) varying the temperature, (*b*) varying the pressure, or (*c*) adding some non-electrolyte to the water. In the case of the first of these methods, variation of temperature, ample data are already available, and the work of Johnston[15] has demonstrated completely the validity of equation (3) in this instance. In searching for a suitable function of temperature to use in plotting ionic conductances at different temperatures for the purpose of interpolation, Johnston discovered that if the logarithms of the equivalent conductances of any ion at different temperatures were plotted against the values of the logarithms of the fluidity of water at these temperatures, a straight-line graph was obtained. In other words, when the fluidity of the medium is altered by a change in temperature, the conductance of an ion changes according to the law, $\Lambda_I = k_I f^{m_I}$. This relation has been found to hold for the temperature range 0° to 156° in the case of fourteen different ions. Values for the fluidity exponents of some of the univalent ions are shown in the following table:

TABLE II.

Ion—	Cs	K	NH_4	Na	Li	Ag	NO_3	Cl	$C_2H_3O_2$
m—	0.842	0.887	0.891	0.97	1.05	0.949	0.807	0.88	1.008

[15] Johnston, J. Amer. Chem. Soc., **31**, 1010 (1909).

The values for Cs and Li are based upon conductance and viscosity data at 0° and 18° only, no measurements at higher temperatures being available.

A glance at this table suggests several interesting relations: (*a*) In no instance does the value of *m* differ from unity by as much as 0.2 (*b*) In the case of the alkali ions the exponent *m* increases with increasing ionic volume, being smallest in the case of the (probably) unhydrated Cs ion and greatest in the case of the highly hydrated Li ion. (*c*) The K ion and Cl ion, which have nearly the same ionic volumes have also the same value for *m*. (*d*) The value for the very large Li ion is greater than unity. These ions possibly resemble most nearly the minute spheres studied by Millikan, and the deviation from Stokes' law is in the same direction as that which he observed. In the case of the other ions their possibly unsymmetrical shape and their much smaller size in comparison with the water molecules combine to produce a smaller increase of mobility with increasing fluidity than Stokes' law requires.

Using the data of Dutoit and Duperthuis on the fluidity and the conductances at zero concentration of sodium iodide in a number of solvents at a series of temperatures between 0° and 80°, Johnston applied the equation $\Lambda = kf^m$, and found that it agreed with the observations in every instance. The values of *m* for the different solvents were as follows: Ethyl alcohol, 0.935; propyl alcohol, 0.974; isobutyl alcohol, 0.955; isoamyl alcohol, 0.806; acetone, 1.086; and pyridine, 0.99.

In the case of the second method of altering the fluidity (by changing the pressure), no data are at present available. In the case of the third one, an isolated example exists in an investigation made by Green[16] of the conductivity and fluidity of solutions of sucrose and lithium chloride in water. Owing to the comparatively high degree of hydration of the ions of this salt, it is not well adapted for testing our equation and we must await the accumulation of further experimental data for different salts and different non-electrolytes before very definite conclusions can be drawn from this method. As far as Green's data are concerned it may be said that they lead to the same value of the fluidity exponent for LiCl as is obtained from the Λ_0

[16] Green, J. Chem. Soc., **93**, 2049 (1908).

values for this salt in pure water at 0° and 18° respectively. To this extent there seems to be satisfactory agreement between the two methods. It is our intention to investigate the subject further in this laboratory, using different salts of the alkali metals as the electrolytes and employing different non-electrolytes to produce the variation in fluidity.

(IV.) Degree of Ionization.

Regarding for the moment the relation, $\Lambda_I = k_I f^{m_I}$, as established, it can be readily shown[17] that the expression for the degree of ionization becomes

$$\gamma = \frac{\Lambda_K}{\Lambda_{oK}} \left(\frac{\eta}{\eta_o}\right)^{m_K} \tag{4}$$

or

$$\gamma = \frac{\Lambda_A}{\Lambda_{oA}} \left(\frac{\eta}{\eta_o}\right)^{m_A} \tag{5}$$

that is, we can compute the degree of ionization of the salt from the equivalent conductance of *either ion-constituent* at the concentration in question (at which concentration the solution has the relative viscosity, η/η_o), the conductance of the ion at infinite dilution, and the fluidity exponent of the ion. It is clear from these equations that in calculating the degree of ionization in a concentrated solution it is the *individual ion-conductances* which must be employed rather than the equivalent conductance of the whole salt. The use of these relations has, consequently, the practical disadvantage that the labor involved in securing the necessary data is considerable. In order to make this clear we will first illustrate the use of these equations by employing them to calculate the degree of ionization, in two examples, after which we will derive an approximate equation, sufficiently exact for most cases, which obviates the necessity of employing the *separate ion-conductances* and permits us to make use of the equivalent conductance of the *salt,* as in the case of dilute solutions.

Degree of Ionization of 0.3 normal LiCl at 18°: Owing to the high degree of hydration of the lithium ion, it is better to employ the chloride ion in making the calculation. The fluidity exponent for this ion is, $m_{Cl^-} = 0.88$ and its equivalent conductance at

[17] The derivation can be found in J. Amer. Chem. Soc., **33**, 1469 (1911).

infinite dilution is, $\Lambda_{o_{Cl^-}} = 65.5$ (Kohlrausch). To find its conductance, Λ_{Cl^-}, in 0.3 normal LiCl solution, we must multiply the conductance of the salt at this concentration, Λ_{o_3}, (= 74.88, Kohlrausch), by the true transference number, T_{Cl}, of the chloride ion. To obtain the latter quantity we must make use of the relation

$$T^{Tr}_{Cl^-} = T_{Cl^-} - \triangle No \frac{N}{No} \qquad (6)$$

in which T_{Cl^-} (= 0.701) is the ordinary or Hittorf transference number of the chloride ion, $\frac{N}{No}$ (= 0.0056) is the molecular ratio, $LiCl/H_2O$, in the solution, and $\triangle No$ is the number of moles of water transferred from anode to cathode per Faraday of electricity. *No* for 0.3 normal LiCl at 18° has not been measured. For a 1.2 normal solution at 25° this quantity has been found by the writer[18] to be 1.5 moles and since it occurs only in a correction term, no large error will be introduced if we employ this value in the present instance. The value of the correction term is, therefore, 1.5 x 0.0056 = 0.0085 and $T^{Tr}_{Cl^-}$ = 0.701 — 0.009 = 0.692. The relative viscosity, η/η_o, of a 0.3 normal LiCl solution at 18° is 1.046 (Grüneisen). Substituting these data in equation (5) we have

$$\gamma = \frac{\Lambda_{Cl}}{\Lambda_{oCl^-}}\left(\frac{\eta}{\eta_o}\right)^{m_{Cl^-}} = \frac{0.692 \times 74.88}{65.5}(1.046)^{0.88} = 0.82$$

The Degree of Ionization of 0.1 Normal Hydrochloric Acid at 25°: The relation, $\Lambda_I = k_I f^{m_I}$, does not hold even approximately in the case of hydrogen or hydroxyl-ion, probably owing to a Grotthus-chain action by means of the water molecules. In employing the relation, $\gamma = \frac{\Lambda_I}{\Lambda_{oI}}\left(\frac{\eta}{\eta_o}\right)^{m_I}$ for calculating the degree of ionization of an acid or a base, therefore, we can use only the anion in the case of the acid and only the cation in the case of the base. Thus for 0.1 normal HCl at 25° we have

$$\gamma = \frac{\Lambda_{Cl^-}}{\Lambda_{oCl^-}}\left(\frac{\eta}{\eta_o}\right)^{m^{Cl^-}} = \frac{0.172 \times 390.4}{75.5}(1.007)^{0.88} = 0.895$$

[18] Washburn, J. Amer. Chem. Soc., **31**, 345 (1909).

The transference number 0.172 is interpolated from the data of Noyes and Sammet.[19] The equivalent conductance, 390.4, is that obtained by Bray and Hunt,[20] and the viscosity is interpolated from the data of Reyher.[21]

The calculation of the degree of ionization of 0.1 normal hydrochloric acid in this manner gives, of course, practically the same result as is obtained by the usual method if, as suggested by Noyes and Sammet, we employ 440.7 as the Λ_o value of HCl at 25°; since, except for the viscosity correction, which at 0.1 normal amounts to only 0.5 percent, the two methods are substantially identical in principle.

An Approximate Expression for γ: The above examples show that the practical objection to the use of the above relation for calculating the degree of ionization of a concentrated solution is the necessity of knowing the true transference number at the concentration and temperature in question. This quantity is difficult to measure and has thus far been determined for not more than four electrolytes, at one concentration and temperature. This method of calculating degree of ionization is, therefore, not capable of a very extensive application with the data at present available.

The necessity of knowing the transference number can, however, be dispensed with if we employ the approximate relation

$$\gamma = \frac{\Lambda}{\Lambda_o}\left(\frac{\eta}{\eta_o}\right)^m \qquad (7)$$

in which $\frac{\Lambda}{\Lambda_o}$ is the usual equivalent conductance ratio of the *salt,* and m the fluidity exponent of the *salt,* has a value intermediate between the fluidity exponents of its two ions. This equation is derivable from equations (4) and (5) on certain assumptions,[17] and it will give sufficiently exact results (0.1 percent) for *most* uni-univalent salts up to normal concentration. It cannot, however, be employed for acids or alkalies and even in the case of certain salts, such as

[19] See Noyes and Falk, J. Amer. Chem. Soc., **33**, 1454 (1911). The correction factor, $\Delta N_0 \frac{N}{N_0}$, is negligible in this instance.

[20] Bray and Hunt, *Ibid,* **33**, 787 (1911).

[21] Reyher, Z. Phys. Chem. **2**, 744 (1888).

lithium chloride, it may give a result which differs by as much as two percent from that given by the more exact expression, equation (5).

The foregoing discussion illustrates a method of procedure by which the viscosity factor can be taken account of and corrected for. This procedure, however, neglects the other factors which affect the conductance in concentrated solutions, and hence a corresponding error in the value of γ may be introduced. To some extent the error from these sources can be eliminated by using the proper method for determining the fluidity exponent, but it is obviously desirable to study separately the effects of the other factors and to determine their magnitudes as far as possible. We will take them up in order beginning with the complex-ion factor.

(V.) Complex Ions.

If appreciable quantities of complex ions of the type $[(KCl)_x K]^+$ and $[(KCl)_y Cl]^-$ are present in the more concentrated solutions they may in general be expected to exercise a pronounced effect upon the true transference number. To obtain this transference number for a concentrated solution of a salt, transference experiments in the presence of a suitable non-electrolyte as a reference substance are necessary. If complex ions are present, the transference number thus obtained will in general[22] differ from the value obtained with a dilute solution of the salt in a medium of the same viscosity. This latter value may be either determined directly or calculated on the basis of the relation, $\Lambda = kf^m$. The former method is, of course, preferable, and in carrying it out the proper viscosity should be obtained by adding to the dilute salt solution the necessary amount of the same material which is used as the reference substance in the experiments with the concentrated solution.

On the basis of the relation, $\Lambda = kf^m$, the equation connecting the true transference number, T_A^{Tr}, of the anion of a salt in a solution of viscosity, η/η_o, with the corresponding value, To_A, at infinite dilution at the same temperature is[23]

[22] It is of course mathematically possible, but not very probable, that x and y in the above formulas for the complex ions might have values such that the transference number would not be affected by the formation of these complexes.

[23] The derivation of this relation has been given in the previous paper (*loc. cit.* p. 1476). Through an error in copying, the sign of the exponent, $(m\text{-}m_A)$, was reversed as given there. The above form is the correct one.

$$T_A^{Tr} = To_A\ (\eta\,\eta_o)^{m-m_A} \qquad (8)$$

where m is the fluidity exponent of the *salt* and m_A that of the *anion*. Since this relation is based upon the equation $\Lambda = kf^m$., it may be used to advantage in studying the latter relation in some instances, especially in the case of acids and alkalies, where it is the only method available, and in the case of salts such as lithium chloride where one ion is highly hydrated.

At the present time there is very little evidence bearing upon the question of the extent to which complex ions of this character may be present in solutions of uni-univalent salts. A systematic study of transference numbers in solution of the alkali halides and nitrates has been undertaken in this laboratory, beginning with caesium salts. The results of the first few experiments point strongly to the existence of very appreciable quantities of such ions in a half normal solution of caesium iodide, and if these results are confirmed by further experiments with the other salts, it means that the complex ion factor is one of the chief ones to be reckoned with. It should be remembered, however, that caesium iodide is the one salt above all others of this group in which we should expect to find the complex ion formation at its maximum. The presence of appreciable quantities of such ions will invalidate equation (7) and make necessary the employment of equation (4) or (5) in calculating the degree of ionization.

(VI.) Decrease in Hydration.

The effect of this factor upon conductance is opposite to that of the preceding one. It may be expected to be most apparent in the case of highly hydrated ions. It may be detected and its magnitude estimated by the determination of the water transferred with the current in solutions of different concentrations. It may also be detected by conductance, or more conclusively by transference experiments with solutions in which the viscosity is the same but the ratio of salt to water and the vapor pressure of the water are allowed to vary. There is some evidence that this factor may exert an appreciable influence in the case of LiCl solutions. Thus the experiments of Green referred to above indicate that the conductance of LiCl chloride solutions containing sucrose increases with decreasing sucrose content faster than would be expected from the relation $\Lambda = kf^m$. This

deviation is in the direction which would result from a decreasing hydration of the Li-ion. Further confirmation is needed, however, before a definite decision on this point can be reached. Some experiments to be undertaken shortly in this laboratory will, it is hoped, throw some further light upon this point.

(VII.) The Grotthus—Chain Effect.

If a potassium ion moving through a potassium chloride solution meets an un-ionized KCl molecule in such a direction that it collides with the chlorine atom, it may unite with it and the other potassium atom may be thrown off from the opposite side as an ion. Such an action would result in a decrease in the path which the ion has to travel between the electrodes and would make itself evident by an increased conductance. A Grotthus-chain effect of this character has been suggested by Daneel[24] as the explanation of the exceptionally high velocities of the hydrogen and hydroxyl ions in water and it has been shown by Hantzsch and Caldwell[25] that in solutions in pyridine, formic acid, acetic acid, hydrobromic acid or sulphuric acid, ions common to the solvent have also exceptionally high mobilities. The magnitude of this effect in the case of a normal salt solution in water is difficult to estimate with any degree of certainity. Its maximum amount may perhaps, however, be roughly approximated by means of the following speculation:

The equivalent conductances of most of the monatomic ions of uni-univalent salts at 18° lie between 60 and 70 while that of the hydroxyl ion is 172, that is, from 2½ to 3 times the value which it would normally have if it moved through the whole distance between the electrodes. If we imagine one liter of a solution containing one equivalent of hydroxl ion placed between two parallel electrodes one centimeter apart, we shall have $\frac{1000}{18} N = 55 N$ molecules of water between the electrodes, where N is the number of molecules in one gram mole. Let us imagine that the conductance of this solution is increased 3 fold by a Grotthus-chain action with the water molecules, that is, that the presence of 55 N molecules between the electrodes practically

[24] Daneel, Z. Elektrochem. **11**, 249 (1905).
[25] Hantsch and Caldwell, Z. Phys. Chem. **58**, 575 (1907).

shortens the distance between them by ⅔ of a centimeter. Now if we imagine a similar solution containing one mole of salt per liter we shall have between the electrodes 0.3 *N* un-ionized salt molecules, if the salt is 70 percent ionized at this concentration. If we assume that the effective reduction of the distance between the electrodes is proportional to the number of un-ionized molecules which take part in the Grotthus-chain action, we should have in the case of the salt solution a maximum reduction of $\frac{0.3}{55} \times \frac{2}{3} = 0.0036$ cm. This would amount to an increase in the equivalent conductance of about 0.4 percent. It seems probable, therefore, that the Grotthus-chain effect will not influence the conductance of a normal salt solution by more than say one percent.

(VIII.) Increased Ionization of the Water.

It has been suggested by several investigators[26] as a probable explanation of some anomalies regarding salt solutions that the presence of considerable quantities of neutral salts in solution causes a large increase in the degree of ionization of the water. The question which we have to consider in the present connection is whether such an increase, if it occurs, will be large enough to affect the conductance of a normal salt solution by say 0.1 percent.

If we adopt 30 as a minimum value for the equivalent conductance of a normal solution of a uni-univalent salt at 18°, we can readily calculate that in order to influence this conductance by 0.1 percent, the specific conductance of the water must be increased about 1,000 fold by the presence of the salt, or in other words that the ionization constant (ion-product) of water must undergo a 600,000 fold increase. Now we have the following abundant evidence that no increase of any such magnitude as this occurs:

1. The substantial agreement between the value of the ion-product for water obtained by Kohlrausch from conductance measurements on pure water and the value obtained from the hydrolysis of salts in 0.1 normal solutions, indicates that the

[26] See for example, LeBlanc, Z. phys. chem. 8, 314 (1891); A. A. Noyes, *Ibid*, 9, 614 (1892); and especially Lewis and Wheeler, *loc cit.*, p. 430.

presence of the salt has practically no effect at this concentration and makes it highly improbable that at higher concentrations any effect of the magnitude stated above can be present.

2. In a paper[27] entitled, "Is Water an Electrolyte," Walden has brought together the conductance data which have been obtained for solutions of small amounts of water in the solvents, H_2SO_4, HCOOH, $(CH_3)_2N\text{-}NO$, $HCONH_2$ and HCN, together with the viscosities and dielectric constants of these solvents. His conclusions regarding the tendency of water to dissociate as an electrolyte are as follows:

(a) "When the most favorable *physical* conditions are chosen —the highest dielectric constant and the highest fluidity of the solvent—water dissolved in such a fluid is generally not a good electrolyte, because the values of the conductivity are either zero or very small."

(b) "Water becomes, however, a good or a better electrolyte when the chemical nature of the solvent is distinctly acid or basic; it is, therefore, fair to assume that the amphoteric water must previously form with the solvent a kind of 'salt,' which is then the conductor of the electric current and an electrolyte." From these results we should evidently not expect the ionization of water to be greatly increased by the presence of a neutral salt.

3. The problem has recently been directly attacked by Poma and Tanzi[28] by measurements of the E. M. F. of the acid-alkali cell. Using the hydrogen electrode they measured the E. M. F. of the combination

$$+ H_2 \left| \begin{matrix} HX \\ MX \end{matrix} \right| KCl \left| \begin{matrix} MOH \\ MX \end{matrix} \right| H_2 -$$

The concentrations of the acid and alkali were the same, being 0.05, 0.1 and 1.0 normal respectively in the different series of measurements. The concentrations of the added salt were also the same on both sides of the cell, and varied in the different experiments from 0 to 2.55 normal. Their results show con-

[27] Walden, Trans. Faraday Soc., **6**, 7 (1910).

[28] Poma and Tanzi, "Über den Einfluss der Elektrolyte auf die Dissociationskonstante des Wassers," Z. phys. chem. **79**, 55 (1912).

clusively that not only is there no large increase in the ionization constant of the water in the presence of neutral salts, but on the contrary there seems to be a decided *decrease*.

We may safely conclude, therefore, that the ions of water cannot produce an appreciable effect upon the conductance of concentrated salt solutions.

In conclusion, we may sum up the situation regarding concentrated solutions of electrolytes as follows:

The problem of extending the Ionic Theory so that it shall be capable of describing quantitatively the behavior of solutions of electrolytes between 0.1 and (say) 1.0 normal with a certainty equal to that with which it can now be applied to such solutions below 0.1 normal, is primarily a problem of the systematic accumulation of the necessary experimental data. By this I mean that the general features of the problem and the factors involved in it are fairly well understood. We know just what data we need and how to go about it to obtain them. Radically new methods of attack will not be needed, and although some modifications of present experimental methods will be necessary, the nature of many of these can be foreseen, even at the present time. Our position may be compared to that of a traveler at the borders of a region with the details of whose topography, soil, climate, etc., he is not familiar, but of which he has a pretty good idea of the general 'lay of the land,' so that he is able to plan his campaign intelligently and systematically and conduct it with a minimum expenditure of energy and resources.

Laboratory of Physical Chemistry,
University of Illinois,
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A GENERAL LAW OF IONIZATION FOR SOLUTIONS OF BINARY ELECTROLYTES.

By WILLIAM C. BRAY.
[A summary of an investigation by CHARLES A. KRAUS and WILLIAM C. BRAY.]

The general law which I shall briefly discuss this afternoon was first stated over four years ago by Dr. C. A. Kraus as the result of a preliminary examination of available conductance data in various solvents. During the past year this work has been again taken up, the earlier calculations have been verified and extended by Dr. Kraus and myself, and many striking confirmations of the law have been found. The general relation has the form

$$\frac{(C\gamma)^2}{C(1-\gamma)} = K + D\,(C\gamma)^m \qquad (I)$$

Where C is the concentration of the electrolyte, γ is the degree of ionization calculated from the conductance ratio λ/λ_0, $C\gamma$ is the equivalent ion-concentration and K, D and m are constants. The investigation has been restricted, for the present, to electrolytes which are capable of dissociating into two univalent ions, for the reason that the law of ionization of electrolytes of higher valence types appears to be more complex[1] than that of simple binary electrolytes, $AB \leftrightarrows A^- + B^+$

The significance of the relation (I) is most easily understood by considering separately the two terms on the right hand side of the equation. The first term gives the familiar relation predicted by the law of mass action for a binary electrolyte,

$$\frac{(A^-)(B^+)}{(AB)} = \frac{(C\gamma)^2}{C(1-\gamma)} = K \qquad (II)$$

The second term is easily reduced to the well known empirical law for the ionization of aqueous solutions of strong electrolytes,[2]

[1] There is evidence that uni-bivalent salts such as $CaCl_2$, dissociate in steps.

[2] In aqueous solutions the exponent $2-m$ usually has the value 1.5 ± 0.1, and m is therefore equal to 0.5 ± 0.1.

$$\frac{(C\gamma)^{z-m}}{C\,(1-\gamma)} = D \qquad \text{(III)}$$

The relative values of the two terms is seen to depend on the ion-concentration $(C\gamma)$; and as the ion-concentration decreases, the second term, $D(C\gamma)^m$, must ultimately become negligible in comparison with the first term, the constant K. Stating these results in another way, we have the fundamental ideas upon which relation (I) is based: (1) that the law of mass action holds when the solution is sufficiently dilute, and (2) that the deviation from the mass law may be expressed as an exponential function of the ion-concentration.

The idea that the law of mass action (II) must hold at sufficiently high dilution, even in the case of strong electrolytes, has received far too little attention. If the ionic theory has any real significance, we must regard the ions, A^-, B^+, and the unionized substance, AB, as chemical individuals, and conclude that the laws of chemical equilbrium must be applicable when the solution is sufficiently dilute.

The experimental evidence that the mass law is obeyed in dilute solutions is furnished by the results of E. C. Franklin and C. A. Kraus obtained with a large number of inorganic and organic electrolytes in liquid ammonia, and those of Dutoit and his associates with a few salts in propyl, butyl and amyl alcohols, acetone, pyridin, sulfur dioxide and some other solvents. The first-named investigators suggested that the mass law was obeyed in dilute solutions, and Dutoit is a strong advocate of this idea; but their careful measurements have not received the attention to which they are entitled. In these investigations there are a number of instances in which specific results have been checked by independent work, but the chief evidence of accuracy lies in the concordant nature of the results as shown by graphical methods of representation. In this connection it is worth noting that Dutoit and his associates appear to have used graphical methods only infrequently, and that the graphs employed by Franklin and Kraus are different from those used by Dr. Kraus and myself in the present investigation.

To examine graphically whether or not the mass law is obeyed in dilute solution, values of $1/\lambda$ were plotted as ordinates and

of $C\lambda$ as abscissae. Since the mass law relation (II) may be transformed into

$$\frac{1}{\lambda} = \frac{1}{\lambda_o} + \left(\frac{1}{K\lambda_o^2}\right)(C\lambda) \qquad \text{(IV)}$$

it is evident that a straight line will result if the mass law is obeyed, that the intercept on the $1/\lambda$-axis gives the value of $1/\lambda_0$ and that the mass law constant K can be calculated from the slope of the line. This relationship has been found to hold in a large number of examples, and has in general proved most satisfactory when the separate results were concordant among themselves.

TABLE I.

RESULTS IN ACETONE AS SOLVENT. (Dutoit and Levier.)

(*A*) *Preliminary* λ_0 *Values.* (Siemens' units).

	NH_4	K	Na	Li
SCN	172 ± 3	169 ± 1	. . .	169 ± 3
I	160 ± 1	156 ± 1	156.5 ± 1	155 ± 1
Br	157 ± 6	157 ± 1	156 ± 1	154 ± 1

(*B*) *Adopted* λ_0 *Values.*

	NH_4	K	Na	Li
SCN	172	169	169	167
I	159	156	156	154
Br	159	156	156	154

(*C*) *Values of* $K \times 10^4$.

	K	Na	Li	NH_4
I	51	40	31	15
SCN	31	. .	18	8.3
Br	16	13	5·7	2.3

The nature of the results obtained is shown in Table I,—for a series of salts in acetone as solvent, based on the experimental work of Dutoit and Levier. Similar results have been obtained in pyridin and even more comprehensive ones in liquid ammonia. In Table I (*A*) are given the 'preliminary' λ_0-values[3] obtained graphically for each separate salt, and also an estimate of the possible error in λ_0 based on the deviation of the separate experimental points from the smooth curve. Table I (*B*) contains the 'adopted' λ_0-values, which are concordant for all the salts, and Table I (*C*) shows the values of K derived from these

new λ_0-values with the aid of the $1/\lambda$, $C\lambda$ diagram. The excellent agreement between the two sets of λ_0 values in Tables I (A) and I (B) furnishes a verification of the Kohlrausch Law of the additivity of ionic conductances, or, if this law is accepted, the agreement is a striking proof of the accuracy of the experimental results.

In Table I (C) the great variation in the values of K for the different salts should be noted. For the iodides there is a regular decrease in the order; potassium, sodium, lithium, and ammonium. For the lithium salts K for LiBr is over five times smaller than that for LiI, and a five fold variation in K corresponds to a very large difference in the degrees of ionization at a given salt concentration. The value of K for LiCl, calculated from the results of Dutoit and Benz, was also found to be less than one-fifth that for LiBr. As a further illustration, the values of K for a few of the electrolytes[4] which have been investigated in liquid ammonia are given in Table II. It is evident that no sharp division into strong and weak electrolytes is possible in these solvents. We have found, moreover, that, in a given series of salts, as the iodides, the values of K do not always lie in the same order in different solvents.

TABLE II.

VALUES OF K AND λ_0 IN LIQUID NH_3 AT — 33.5° C.

Solute	λ_0	$K \times 10^4$
Cyanacetamid	ca 260	ca 0.05
Ortho-methoxy-benzene sulfonamid	208	0.41
Para-methoxy-benzene sulfonamid	208	0.50
Meta-methoxy-benzene sulfonamid	208	1.9
Meta nitro-benzene sulfonamid	230	13.7
KNH_2	301	1.2
AgI	287	3.1
NaCl	310	14.
$NaNO_3$	301	23.
NaBr	302	27.
NaI	301	30.

[3] Nearly all of the results of Dutoit and his associates have been expressed in Siemens' units. In Table I the θ_0 values have been left in these units, but in the other tables the factor 1.069 has been used to change to the ordinary units.

[4] In the case of the organic substances in Table II, the positive ion is undoubtedly NH_4.+ From Franklin and Cady's transference measurements NH_4+ was calculated to be 131.

These irregular variations in the values of K render it difficult to find a satisfactory method of comparing the ionizing power of different solvents. The natural method is to compare in different solvents the values of K for a single salt, but this involves the arbitrary and very questionable assumption that this salt behaves as a "typical" salt in each solvent. Such a comparison has been made in Table III, chiefly with the salt NaI as solute. This salt appears to be as nearly "typical" as any we can hope to find, and this is undoubtedly connected with the fact that, in any solvent, iodides and sodium salts are, in general, relatively highly ionized.

Table III.

Values of K and λ_0 in Various Solvents.

Solvent	Solute	Investigators	Temp.	λ_0	$K \times 10^4$	Dielectric Const.
Water	KCl	Kohlrausch and Maltby	18°	129.8	ca 200	80
Benzonitril	NaI	Dutoit and Nicollier	25°	49.	ca 55	26
Propyl alcohol	NaI	Dutoit and Ottiker	18°	20.6	45	23
Acetone	NaI	Dutoit and Levier	18°	167.	40	22
Acetophenone	NaI	Dutoit and Nicollier	25°	35.	44	19
Ammonia	NaI	Franklin and Kraus	—33.5°	301.	30	19
Methyl ethyl ketone	NaI	Dutoit and Nicollier	25°	139.	25	18
Isobutyl alcohol	NaI	Dutoit and Gagnaux	25°	13.7	12	18
Aceto acetic ester	NaI	Dutoit and Gagnaux	18°	30.7	ca 15	16
Pyridin	NaI	Dutoit and Ottiker	18°	61.5	11	12
Isoamyl alcohol	NaI	Dutoit and Gagnaux	25°	9.5	4.	15
Pyridin	KI	Dutoit and Ottiker	18°	64.	5.	12
Sulfur dioxide	KI	Franklin	—10°	207.	7.	15
			+10°	240.	4.	15

In the $1/\lambda$, $C\lambda$ diagram already referred to, the straight line from which λ_0 and K are determined always rises with increasing values of $C\lambda$; the smooth curve through the experimental points coincides with this straight line for very dilute solutions and always lies below it for higher values of $C\lambda$. The value of $C\lambda$, at which the divergence of the smooth curve from the straight line is appreciable in the diagram, can be read off from the plot, and the corresponding value of $C\gamma$ is the ion-concentration above which the deviations from the mass law exceed a percentage value which may be determined from the plot. This "limiting" value of $C\lambda$ was determined for all the substances shown in Table II, except cyanacetamid, and was found always to lie in the neighborhood of 2×10^{-4}. Similarly, in the solvent acetone,

this "limiting" ion-concentration for NaI was about 4×10^{-4}, and in none of the cases shown in Table III was the value greater than 10^{-3}.

This fact, that the mass law does not hold except below such extremely small ion-concentrations, is one of the most striking results of this investigation. It is important also to note that the determining factor is the ion-concentration and not the salt-concentration. For relatively-slightly ionized substances the mass law may hold up to high concentrations of the solute, as in the case of the so-called weak electrolytes in water.

When the small value of these "limiting" ion-concentrations is considered, it is easy to understand why the law of mass action has not been shown to hold in dilute aqueous solutions of strong electrolytes. Owing to the high specific conductance of water (it is much higher than that of liquid ammonia, acetone, etc.), it is extremely difficult to make accurate measurements at concentrations less than 10^{-3}. Moreover, on account of the high ionization of the salts, the concentration of the un-ionized substance cannot be accurately determined and the values of K calculated for very dilute solutions have no significance.[5] The possibility of testing the mass law in other solvents depends on the small specific conductance of the pure solvent, and on the fact that in moderately dilute solutions the ionization is neither too large nor too small. At the same time, we must not lose sight of the great difficulty of making accurate measurements at dilutions between 10^3 and 10^5 liters, and we must admit that our present results may be appreciably altered by a repetition of the experimental work or by a revision of the calculations.

The percentage error in the values of λ_0 is probably small, but that in the values of K may be large. Since also, there may have been a tendency on our part to make the mass law hold to as high concentrations as possible, it is probable that the "limiting" ion-concentrations given above are too large rather than too small.

In the last column of Table III, approximate values of the dielectric constants of the various solvents have been collected. Comparison with the values of the mass law constant K shows that there is a general parallelism between the two quantities, and

[5] The value of K for KCl in Table III is an approximate value determined by means of the complete equation (I), (see Table V), and is inserted to show that K is greater in water than in other solvents.

that K decreases more rapidly than the dielectric constant. This is a very striking illustration of the Thomson-Nernst rule that the ionizing power of a solvent is related to its dielectric properties. It is evident that, in solvents with much lower dielectric constants than those shown in Table III, the values of K for even the most highly ionizable salts will be very small. This corresponds with the experimental fact that in such solvents the conductivity of a dilute salt solution is extremely small. In a few such cases there is evidence, in case of dilute solutions, of an increase of the equivalent conductance λ with increasing dilution, but it will, in general, be impossible to make accurate measurements in sufficiently dilute solutions to enable λ_0 and K to be determined by the graphical method described above. In these cases, in moderately concentrated solutions, K may be neglected and the nature of the second term of the general equation (I) may be directly determined.

The experimental results with these solvents show that in moderately concentrated solutions the equivalent conductance λ increases with increasing concentration. These examples have frequently been cited to disprove the ionic theory, and as exceptions to the Thomson-Nernst rule. On examining these results, we have found in each case, for a considerable range of concentration, that λ is proportional to some power of $C\lambda$; or, multiplying both sides by $C\lambda$, we have found that $C\lambda^2$ is proportional to $(C\lambda)^m$. That this is directly related to the general equation (I) or to the empirical equation for aqueous solutions (III), is seen by neglecting K in (I) and substituting λ/λ_0 for γ. We then obtain

$$C\lambda^2 = D\lambda_0^{1-m}(\lambda_0 - \lambda)(C\lambda)^m$$

The proportionality factor of the right hand member is practically a constant, differing but little from $D\lambda_0^{2-m}$ when λ is small compared with λ_0, as is often the case. This relationship was tested graphically by plotting log (λ) or log $(C\lambda^2)$ against log $(C\lambda.)$, and showing that, for a large range of concentrations, the experimental points lie very close to a straight line. At one end of the line there were deviations in one direction, owing to the fact that K was no longer negligible, and at the other end there were definite deviations which will be discussed later.

Approximate values of m and of $D\lambda_0^{2-m}$ were determined from the plots, and a few of the results obtained are shown in Table IV.

From these and other similar results it has been possible to draw the conclusion that m is always greater than unity in solvents with low dielectric constants, and it seems not improbable that 2 is the highest value that can be reached in a solvent of very low dielectric constant.

We have thus shown that there are a large number of examples in which the two parts of the general relation, shown in equations (II) and (III), are separately applicable. The final tests of the relation were made with the comprehensive data of Franklin

Table IV.

Approximate Values of m and $D\lambda_0^{2-m}$.

Solvent	Dielectric Const.	Solute	Investigator	Temp.	m	$D\lambda_0^{2-m}$
Ethylamine	6	$AgNO_3$	Shinn	0°	1.39	4.5
Amylamine	5	$AgNO_3$	Kahlenberg and Ruhoff	25°	1.68	1.86
Hydrochloric acid	9	Ether	McIntosh and Archibald	—100°	1.57	1.38
Hydrobromic acid	6	Ether	McIntosh and Archibald	—81°	1.62	0.56
Hydriodic acid..	3	Ether	McIntosh and Archibald	—50°	1.66	1.32
		$(C_2H_5)_3NHCl$	McIntosh and Archibald	—50°	1.64	3.1
Hydrogen sulfide.	—	$(C_2H_5)_3NHCl$	McIntosh and Archibald	—81°	1.56	2.0
Iodine	—	KI	Lewis and Wheeler	140°	1.54	16.
Anilin	7.2	$C_5H_5N.HBr$	Sakhanov	25°	1.50	2.0
Methylanilin ...	5.3	$C_5H_5N.HBr$	Sakhanov	25°	1.60	0.63
Acetic acid	6.5	C_5H_5N	Sakhanov	25°	1.55	1.88
		LiBr	Sakhanov	25°	1.46	2.63
Propionic acid ..	3.1	C_5H_5N	Sakhanov	25°	1.75	0.32
		LiBr	Sakhanov	25°	1.73	0.86

and Kraus and of Franklin, using both parts of the equation. In all the cases tested equations of the general form (I) were found which agreed with the conductance data fairly well up to the neighborhood of normal concentration. Within this range the conductance at any concentration can be calculated satisfactorily from the four constants λ_0, K, m, and D. Some preliminary results are shown in Table V. In liquid ammonia the values of m lie between 0.84 and 1.18, and are usually less than 1.0. Comparison with Table IV indicates that for the more highly ionized substances the values of D are not widely different in different solvents.

We are now in a position to examine the nature of the conductivity-concentration curves corresponding to the general relation

(I). The two simplest variables to choose are γ and $C\gamma$, since (I) may be written in the form

$$(C\gamma)\left(\frac{\gamma}{1-\gamma}\right) = K + D\,(C\gamma)^m;$$

and the most convenient co-ordinates are γ and log $C\gamma$, which, of course, correspond exactly to the co-ordinates equivalent conductance and log specific conductance. Curves of the same general form are also obtained on plotting γ or λ against C. λ has its maximum value at infinite dilution and with increasing concentration decreases regularly towards zero when m is less than unity. Whenever m is greater than unity, λ passes through a minimum and then increases. For the intermediate case $m = 1$,

TABLE V.

Solvent	Solute	Temp.	λ_0	$K \times 10^4$	m	D
Water	KCl	18°	129.8	ca 200	0.63	2.5
Ammonia	KNH_2	—33.5°	301	1.2	1.18	0.10
	NH_4Cl	—33.5°	310	12.	0.84	0.13
	KNO_3	—33.5°	339	16.	1.00	0.28
	NH_4NO_3	—33.5°	301	29.	0.90	0.43
	NaI	—33.5°	301	30.	0.87	0.50
Sulfur dioxide	KI	—33.5°	166	11.	1.06	0.36
		—10°	207	7.	1.14	0.40
		+10°	240	4.	1.21	0.43

λ approaches asymptotically a finite value, which depends on the value of D. Examples of all these cases are given in Table V; also in Table IV, where m is greater than unity, there are a number of examples in which the mass-law portion of the curve is missing and in which the conductance decreases with increasing dilution over the whole range of concentrations investigated.

Whether or not the relation (I) proposed is a perfectly general one can only be settled by further investigations. Before its exactness can be accurately tested, some corrections are necessary, of which the most important is that for viscosity. The simplest manner of applying this correction would be to assume a direct proportionality between resistance and viscosity, but unfortunately there are practically no viscosity data for non-aqueous salt solutions. We do know, however, that in some cases the concen-

trated solutions become very viscous and that, in these cases the correction must be very large. This would have the effect of making the measured conductances smaller at high concentrations than would be predicted from the results in less concentrated solutions. Such an effect has been found in concentrated solutions, and has been considered by Franklin and others to be due to the high viscosity of these solutions. It is a general phenomenon which usually appears in the neighborhood of normal concentration, and doubtless corresponds to the deviations from the general law referred to in the discussion of the results in Tables IV and V. It seems probable that, when the viscosity correction is made, the general relation (I) will be found to hold up to much higher concentrations. Deviations are, of course, to be expected in each case when a concentration is reached where effects due to polymerization or to a change in the degree of solvation become sufficiently large.

It must be borne in mind, however, that the viscosity correction can be applied in a simple manner only when the transference number is constant at different concentrations. The whole problem would, in fact, be greatly complicated if the relative velocities of the ions showed a large variation with the concentration. The experimental work of Franklin and Cady proves that the transference number for a number of salts in liquid ammonia is constant up to fairly high concentrations, but additional experimental work in this field would be very valuable.

In the present treatment of the subject, we have considered that the conductance ratio $\lambda/\lambda_0 = \gamma$ is an exact measure of the degree of ionization of the electrolyte, and this is equivalent to assuming that the sum of the conductances of the ions, $\lambda A^- + \lambda B^+$, is constant at all concentrations and equal to λ_0. But we must remember that the general relation (I) depends wholly on conductance measurements and is therefore simply a record of the nature of the variation of conductance with concentration. It is still an open question whether or not the conductance ratio λ/λ_0 is a true measure of ionization. I shall not discuss this question at the present time, but shall merely point out that other explanations are not necessarily excluded by our results.

It is difficult to believe that a relation of such general applicability as the present one should be without a theoretical foundation. The nature of the increase of $(C\gamma)^2/C(1-\gamma)$ indicates that the phenomenon depends upon the electrical forces which come into play in a medium containing charged particles. We have not, as yet, been able to formulate a quantitative theory, and I shall not take the time today to present qualitative ideas. In this connection it is worth noting that our quantitative law is in good agreement with the qualitative idea of self-ionization expressed by Franklin and Kraus and by Franklin, and with that of the relation between the ionizing power and the electrophilic character of the solvent expressed by Lewis and Wheeler.

Finally, even if equation (I) is considered simply as an empirical relation, it is of importance as a means of systematizing the experimental data relating to solutions of electrolytes in various solvents. It has been customary heretofore to divide electrolytic solutions into various classes, as dilute and concentrated solutions, aqueous and non-aqueous solutions, and solutions of strong and weak electrolytes, and to treat these classes without reference to one another; but the existence of a single general relation shows that such classifications are purely arbitrary except in so far as they are related to variations in the values of the constants of equation (I).

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ELECTRICAL EMISSION FROM HEATED SALTS

By C. J. Davisson.

In wondering what aspect of the general topic to which I am to address myself would best serve as a point of departure for this discussion, I have concluded that we can most readily reach the heart of the matter by considering a simple experiment which may be used to illustrate many of the phenomena connected with the emission of electrical charges by heated salts.

Suppose that we have at our disposal an apparatus, including the essential features of the one shown in Fig. 1.

In this diagram two rectangular metallic plates *A* and *B* are shown in section.

A slot is cut in the plate *A* and a platinum strip—shown in section at *S*—is let in flush with the general surface.

This strip is electrically heated and carries on its upper surface the salt to be tested.

The arrangement of the heating circuit is shown in Fig. 2.

A and the heating circuit are electrically connected at the one point *C* and the system so constituted may be held at any desired potential by means of the accumulators shown at *P*.

The plate *B* is well-insulated and connects with one side of a quadrant electrometer, shown at *E*, the other side of the electrometer being earthed. (See Fig. 1.)

The electrometer so arranged indicates the electrical potential of *B*, relative to the earth and if electric charge is being carried to or from *B* the fact is indicated by a change in this potential, the rate of change of potential being proportional to the current.

The dimensions of the apparatus for our present purpose are not very important, but we may suppose the plates to be 10 x 10 cm. and 3 cm. apart, and the strip to be 1 x 5 cm.

Suppose the system, including *B*, is earthed, and that *S* is coated with an inorganic salt; almost any salt will do.

If now the temperature of the strip is raised to 500° C. or 600° C. and the potential of A adjusted to, say, + 200 volts, it will be found on disconnecting B from the earth that it acquires positive potential at a definite rate, indicating that positive charge is being carried to it. The magnitude of this current will ordinarily be of the order 10^{-10} or 10^{-11} amperes.

If the potential of A is changed to — 200 volts it will be found that B acquires a negative charge. The magnitudes of these currents will not, in general, be the same.

A word should be said here about the preparation of the strip. With a fresh strip of platinum, results similar to the ones described would have been obtained even though no salt were placed on it. It has been found, however, that by heating the bare strip at 1,000° or 1,100° C. for twenty-five or thirty hours, the strip being held all the while at a positive potential, the positive current can be reduced to a negligible quantity. This ageing of the strip must always be carried out before the testing of the salt is begun.

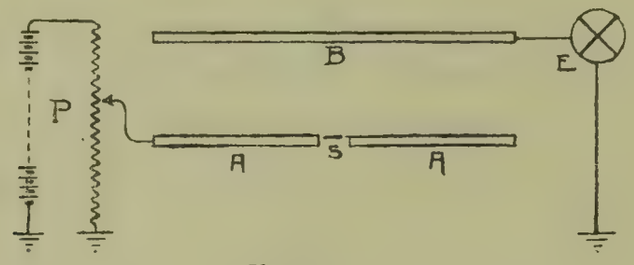

FIG. 1.

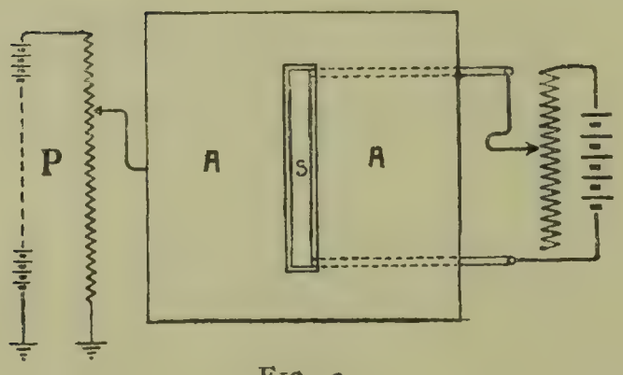

FIG. 2.

The same is not true of the negative current from the bare strip, and for this and other reasons the emission of negative charge (apparent or real) by heated salts has not received the attention which has been paid the positive emission.

As regards the part played by the salt in such experiments as the one just described, the problem before the investigator is to discover and to analyze the mechanism by which charge is conveyed to the plate *B*.

The methods employed in attacking the problem fall naturally under two heads: (I) those which seek to deduce something of the nature of the phenomenon from the variation of the current with one or more of the circumstances upon which it depends; (II) those which seek the same end from data giving direct information concerning the nature of the ions.

I.

Under the first heading the variations which have received attention are the following:

Variation of the current with

(*i*) The nature of the salt.

(*ii*) The potential of the plate *A*.

(*iii*) Time.

(*iv*) The nature and pressure of the gas.

(*v*) The temperature of the strip.

Let us consider briefly these variations in the order set down.

(*i*) Under the first sub-head Garrett, in the Phil. Mag. for 1904, has given us a list of compounds which give rise to apppreciable currents at or below 400° C. and another list of those which do not. It will not be worth while to give these lists.

G. C. Schmidt has recently stated in the "Annalen" that the halogen salts of Zn, Cd, Fe, Al, and ammonium give rise to currents when heated, while similar salts of mercury and of arsenic do not. In the latter group Schmidt also includes tin chloride and all inorganic substances.

So far as Schmidt's and Garrett's tests include the same substances their results are in agreement.

Prof. Richardson has recently stated it as a general rule that those salts give rise to the largest effects which combine volatility with marked electro-positiveness in the metallic ion.

No very great reliance may be placed in the data now available under this head, as facts will be adduced presently to show

that the supposed efficiency of a salt may result from the presence in it of the minutest trace of some impurity.

(*ii*) As regards the variation of the current with the potential of the plate *A*, the experiments of Garrett and Willows, Garrett, Richardson and of Schmidt show that, in general, the current, either positive or negative, increases uniformly with the potential for small values of the latter, increases less rapidly at higher potentials, finally becoming independent of the potential. If the potential is increased indefinitely ions are formed by collision and sparking results.

The exact curves depend largely upon the form of apparatus used. As far as they may be taken to indicate the nature of the phenomenon, they suggest that the current is carried by ions which make their appearance at a definite rate in the space between *A* and *B*.

The relatively high potentials required to saturate the positive current when the gas pressure is high, as well as the particular form of the curves in these cases, further suggest that the positive ions come into existence close to the heated salt, as though they were emitted by it.

The facts that have been adduced in connection with the variation of the current with the time make it seem probable, however, that this emission is in itself a complicated matter, and these facts we shall next consider.

(*iii*) For the first few minutes after the salt is brought to a fixed temperature the current generally increases. After passing through a maximum it decreases, tending to some fixed value —ordinarily not zero.

This fact was first announced by Garrett & Willows in 1904, and has since been verified for a number of salts under a variety of conditions by Garrett, Richardson, Horton and Schmidt.

Garrett has proposed the empirical equation

$$i = A\,(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + B\,(1 - e^{-\lambda_3 t})$$

to express this variation. This equation has a definite meaning in terms of the disintegration theory of radio-active substances, indicating the existence of intermediate transformations preceding ionization.

It may very well be that this analogy to radio-active disintegra-

tion results, in part in least, from a similar mechanism. Richardson has suggested that the ionization may result from the action of the heated surface upon the vapor of the salt, and that in some cases the activity is dependent upon some initial reduction or dissociation of the salt, such, for example, as the initial dissociation of $BaSO_4$ into BaS and $2O_2$.

Processes of this sort together with transient effects due to the heating up of the apparatus may be made to account for practically all time variations, as well as the variations due to the nature and pressure of the surrounding gas, which we shall consider next.

(*iv*) In 1910 Garrett showed that the current from a sample of $AlPO_4$ increases with increasing air pressure up to a pressure of about 2 mm., and that the effect of further increasing the pressure is to diminish the saturation current toward a constant value. He further showed that the maximum in the resulting pressure-current curves occurs at lower and lower pressures as the temperature of the salt is increased.

Similar effects have been noted by Horton and by Richardson for Na_3PO_4 and Na_2SO_4 heated in air, oxygen and carbon monoxide. Horton has found in the case of Na_3PO_4 in hydrogen that although the current increases with the pressure, no maximum is attained up to 20 mm. pressure.

In connection with these and other experiments it has also developed that the nature as well as the pressure of the gas has much to do with the magnitude of the current.

These facts form part of the basis of an hypothesis which regards the current as due to ions derived from the gas. Recent discoveries along these same lines have not, however, tended to strengthen this hypothesis.

Richardson has shown that the pressure-current curves are largely conditioned by the form of the apparatus. Using an apparatus in which the plates *A* and *B* of Fig. 1 are replaced by a tube and a co-axial rod respectively, the salt resting at the bottom of the tube, Richardson has obtained pressure-current curves differing entirely from those obtained by the strip method. In some cases the current increases with the gas pressure, in others it decreases. Sharp maxima and minima are not features of the curves, and on the whole the variations are smaller.

Richardson has further demonstrated that cases exist in which the pressure may be changed suddenly from an atmosphere to a small fraction of a mm. without appreciably affecting the current.

Even by the strip method the maxima in the pressure-current curve may be made to disappear at low temperatures, in some cases by heating the salt for some time at a much higher temperature.

Richardson believes that all such effects, so far observed, may be explained on the general suppositions that the gas acts chemically to facilitate or to retard the formation of ionizable products, and mechanically to hold them near the surface until their ionization is effected. This view receives some support from what seems to be a general rule that the current from oxy-salts is increased by the presence of gases which facilitate their reduction.

(*v*) We have still to consider the variation of the current with the temperature of the salt. Fortunately this variation admits of simple formulation.

Garrett has shown that the positive currents from ZnI_2, CaF_2, AlF_3 and NH_4NO_3, as well as the negative currents from ZnI_2, $FeCl_3$, NH_4Cl, CaF_2, NH_4NO_3 and $MgCl_3$, are expressible for temperatures lying roughly between 200° C. and 400° C. by the equation

$$i = A\,\theta^{1/2}\,e^{-\frac{\rho}{\theta}}$$

i being the current and θ the absolute temperature of the salt.

Current-temperature data for CdI_2, by G. C. Schmidt, shows that this salt also conforms to the rule so far found general.

The formula itself is one which was deduced by Richardson to account for the temperature variation of electrical emission from heated metals. The physical assumptions upon which the deduction is based are two in number: First, that a definite number of charged carriers exist per c.c. in the emitting substance, whose kinetic energy corresponds in amount and distribution to a collection of gas molecules at the same temperature; second, that these charged particles are held in the body by virtue of the fact that work must be done upon them to carry them through the surface against forces residing there.

At any temperature a certain number of carriers escape per second by virtue of favorable opportunity and sufficient kinetic energy. The number escaping per second will evidently be a function of the temperature. The exact function is the one written down.

The fact that this equation does express the relation between the current and the temperature for at least eight different salts would seem to indicate that we are at least near to one fundamental fact concerning the mechanism of the emission.

If, however, we accept this verification of a theoretical formula for its face value, and suppose that the emission occurs in this simple way, we apparently leave unexplained a number of the effects due to time of heating and to the surrounding gas.

The variation of the current with time and the gas have been mostly studied in connection with oxy-salts, while the temperature variations have been studied, with one exception, in connection with halogen salts. It is possible that this may account for the dilemma.

In any case the crying need is for simpler and more systematic data.

II.

Let us turn now to the work which has been done in seeking to gain direct information concerning the nature of the ions.

The experiments of Garrett and Willows, Garrett and Todd, on the velocities of the carriers from a number of halogen salts in hydrogen, marsh gas, air, carbon dioxide and sulphur dioxide, at various pressures, point to the fact that the masses of the carriers are large compared with molecular masses—excepting at the lowest pressures. In this respect they resemble the carriers drawn from salt-laden flames, and the explanation that the large masses of the latter are due to the condensation of the vapor of the salt about the real ions as nuclei may very well apply in this case.

The fact that a simplification of the carriers occurs at low pressures suggests that a determination of e/m for these simplified carriers might be of considerable value.

The methods which have been employed to determine this quantity, which is the reciprocal of the electrochemical equivalent, have been based entirely upon measurements of the magnetic

deflections of the ions moving "in vacuo" under the influence of an electric field.

Garrett employing Thomson's cycloidal method found for e/m (in E. M. units per gram) for the lightest positive carriers from $AlPO_4$ approximately 10^4, from which he concluded that at

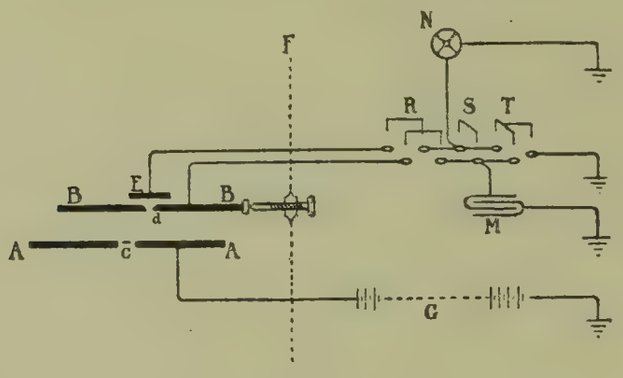

FIG. 3.

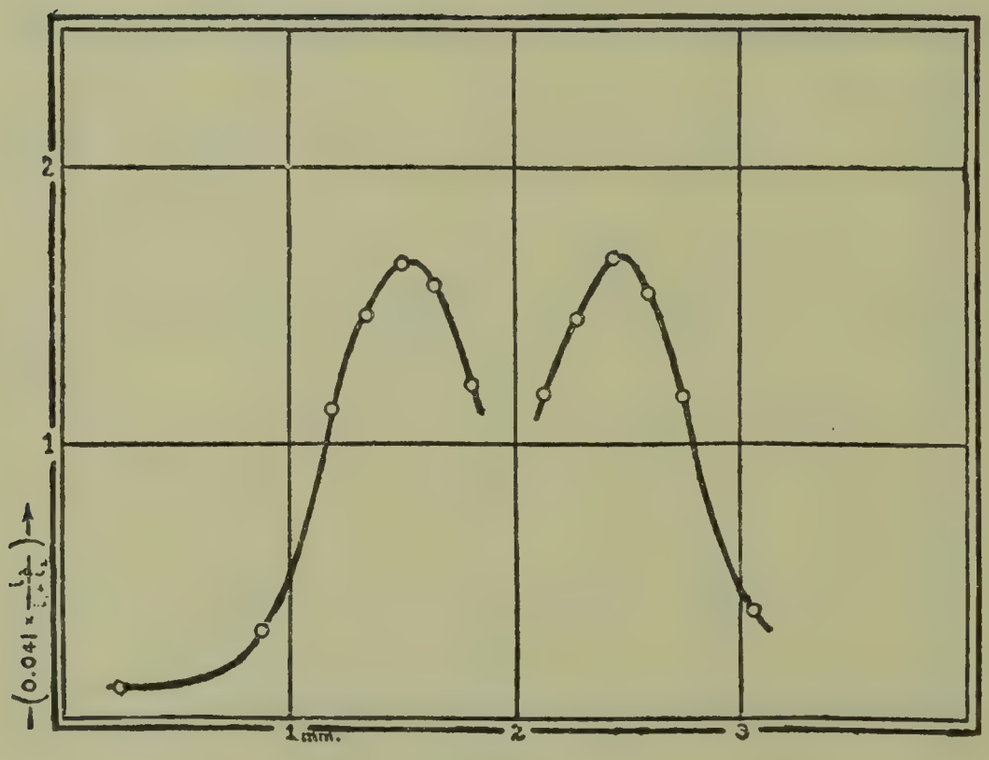

FIG. 4.

least a part of the current is carried by hydrogen ions. This result has been taken to support the gas theory of the emission.

Another experimental result which might be mentioned in this connection is the fact discovered spectroscopically by Horton, that CO accumulated in an exhausted vessel containing a heated salt emitting positive charge.

This fact has also been used to support the gas theory, but

the further fact that the rate of generation of CO is independent of the current shows that the CO probably comes from organic impurities in the salt and is uncharged.

By far the most important determinations of e/m have been made by Richardson. It will be perhaps worth while to look into the method employed in these determinations.

The apparatus, Fig. 3, is similar to the one shown in Figs. 1 and 2, excepting that a slit is cut in the plate B, parallel to the strip, and back of this slit is an additional electrode E which intercepts any of the ions that are projected through. B and E may be moved back and forth at right angles to the length of the slit, and means are provided for measuring the ratio of the current passing through the slit to the total current.

If this ratio is measured for different positions of the slit, while A is held at a high positive potential, the ratio has its maximum value when the slit is just opposite the strip.

If now a magnetic field is established in the space between A and B, the position of the slit for the maximum in the ratio is shifted to the right or to the left, depending upon the direction of the magnetic field.

By making observations with the field first in one direction and then in the other two curves are obtained on the same diagram, such as the ones shown in Fig. 4.

For an apparatus of given dimensions and for given values of the electric and magnetic fields, the distance between the peaks of these curves depends upon the value of e/m for the ions, and from a knowledge of these various physical quantities e/m may be calculated.

By this method Richardson has found the following values for e/m for the positive ions from the sulphates of the alkali metals.

Sub.	E/M	Elec. At. Wt.	Chem. At Wt.
Li_2SO_4	1598	6.2	7.05
Na_2SO_4	430	22.5	23.05
K_2SO_4	264	36.5	39.15
Rb_2SO_4	101	96.0	85.5
Cs_2SO_4	73	140.	132.2

The column of figures marked "Elec. At. Wts." are calculated from the corresponding values of e/m on the assumption

that the ions carry the charge carried by ions of monovalent atoms in electrolysis.

A word should be said about abnormal results, which continually turn up in determinations by this method. It is frequently found that no matter what salt is tested the first values of e/m turn out to be in the neighborhood of either 430 or 260; that is, they correspond approximately to Na or K and are taken to indicate the presence of these substances in the so-called "Chemically Pure" salts. In most cases these values are obtained only at comparatively low temperatures, and as this emission dies away the one which is truly characteristic of the salt puts in its appearance.

Richardson lately showed that the values of e/m for the posi-

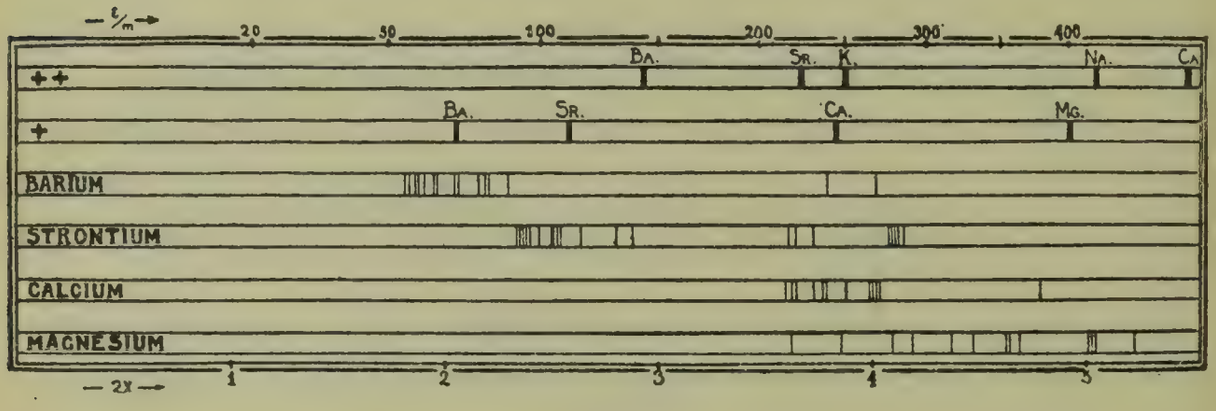

FIG. 5.

tive ions from salts of alkali metals are independent of the nature of the acid radical.

More recently similar experiments have been carried out under Richardson's directions upon the salts of the alkaline earths. The results of these experiments, though not exactly what might be expected, are nevertheless concordant with those previously obtained in the case of the alkali metals. These results are exhibited graphically in Fig. 5.

The scale of $2x$ at the bottom of the figure gives distances between the peaks of the experimental curves.

The scale at the top gives corresponding values of e/m for a particularly chosen set of values for the electric and magnetic fields and for the distance between A and B.

The heavy marks in the first space are placed under the values of e/m for Ba, Sr, etc., carrying double charges.

In the next space the heavy marks correspond to the same elements carrying single charges.

The finer lines in the remaining spaces represent experimental determinations of $2x$ for various salts of the same elements. These results indicate plainly that the ions of the divalent elements carry single charges. It will be noticed in this diagram

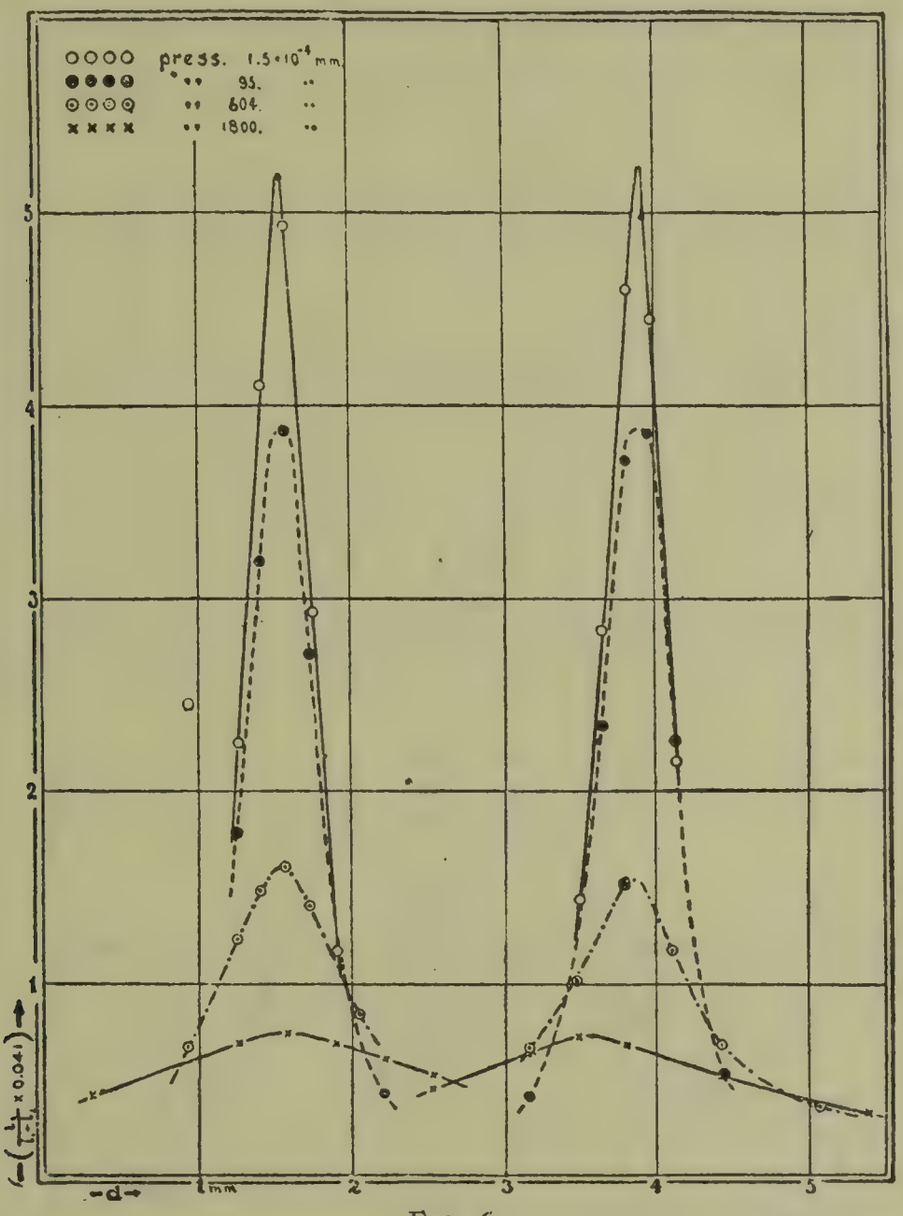

FIG. 6.

that the abnormal values fall mostly in the neighborhood of potassium.

In connection with these same experiments, others were carried out to determine the effect of the pressure and nature of the surrounding gas upon the value of e/m. The determinations so far mentioned were all made at pressures less than 10^{-4} mm. by the McLeod gauge.

What occurs when the pressure of the gas is increased is better illustrated than described. Curves obtained from a sample of $AlPO_4$ are shown in Fig. 6. It will be noticed that the first effect of increasing the pressure of the air is to lower

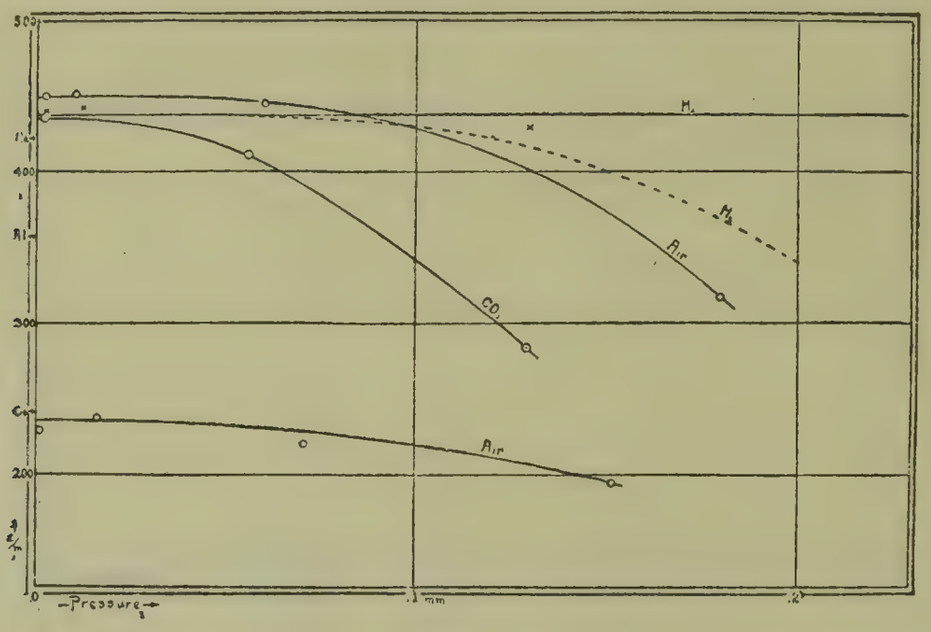

FIG. 7.

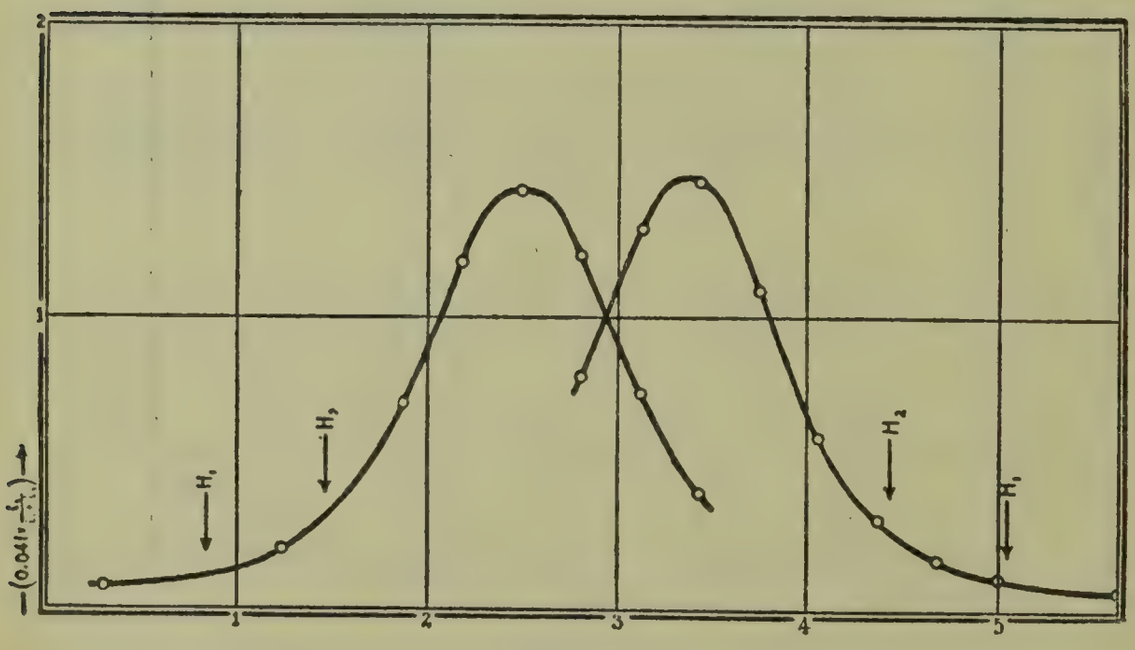

FIG. 8.

and broaden the curves without interfering to any great extent with their relative displacement. As the pressure is further increased, however, the gas interferes with the magnetic deflection and the peaks draw nearer together, resulting in an apparent decrease of e/m.

This latter effect is better shown in Fig. 7, where the apparent values of e/m for the ions from this same sample are plotted against gas pressures.

It will be noticed that for a given pressure CO_2 is most effective in interfering with the magnetic deflection, air next and hydrogen least, as would be expected if the action is purely mechanical.

The values of e/m in each gas at the lowest pressures fall near the value corresponding to Na, and are taken to indicate the emission of that element. It is interesting to note that after a protracted heating this sample finally gave one or two values of e/m corresponding to aluminium carrying a single charge. The one curve at the bottom of the diagram is for $CaSO_4$ in air.

The nature of these curves does not suggest that the current is being carried by ions of the gas. To further test this point, a search has been made for secondary maxima in the curves from $AlPO_4$ in H_2, at a pressure of 1 mm.

The result of the search is shown in Fig. 8. The arrows marked H_1 and H_2 indicate the positions at which secondary maxima would appear if hydrogen atoms or molecules participated in the conduction.

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

ELECTRICAL CONDUCTIVITY OF GASES.

By P. G. Nutting.

The electrical properties of gases conducting an electric current are very different from those of metals or of electrolytes. The ratio of potential gradient to current, instead of being nearly constant, as would accord with Ohm's law, varies enormously with the current density.

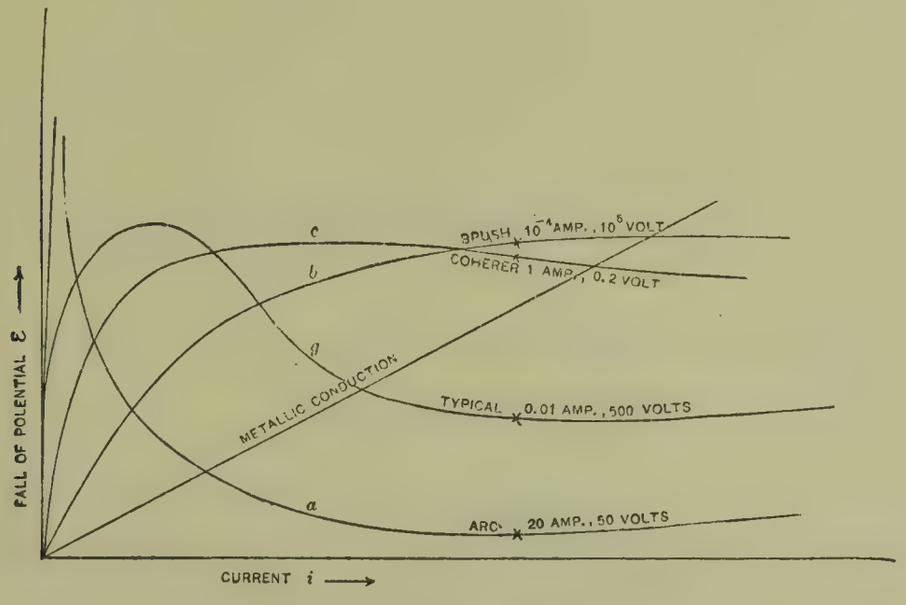

Fig. 1. Characteristic Conduction Curves.

In metals (Fig 1, E (i) metals), the plot of gradient E as a function of current i is practically a straight line over a wide range. Hence we infer that both the number of carriers and the viscous resistance to their motion is constant. The absence of an observable toe to the graph indicates that no energy is required to produce the carriers at the start. The normal rise in the ratio E/i with high current densities may signify either a change in the number of carriers or a decrease in their mobility, due either to current density itself or thermal effects. I am unaware of any attempt to segregate the two effects.

In contrast with this curve for metals the typical curve for gases shows both a maximum and a minimum, due probably to

wide variations in the numbers of the carriers. (Fig. 1, E (i) gases.) Initially there is a rapid rise of gradient with current, carriers are few and large and move with great difficulty. With still greater potential gradients the carriers move independently with high velocity and by collision produce other carriers. The ratio of E to i falls rapidly, and if the gas is at low pressure or if the electrodes are very hot, as in the arc, may fall to a very low value. At very high currents the gradient again increases with current.

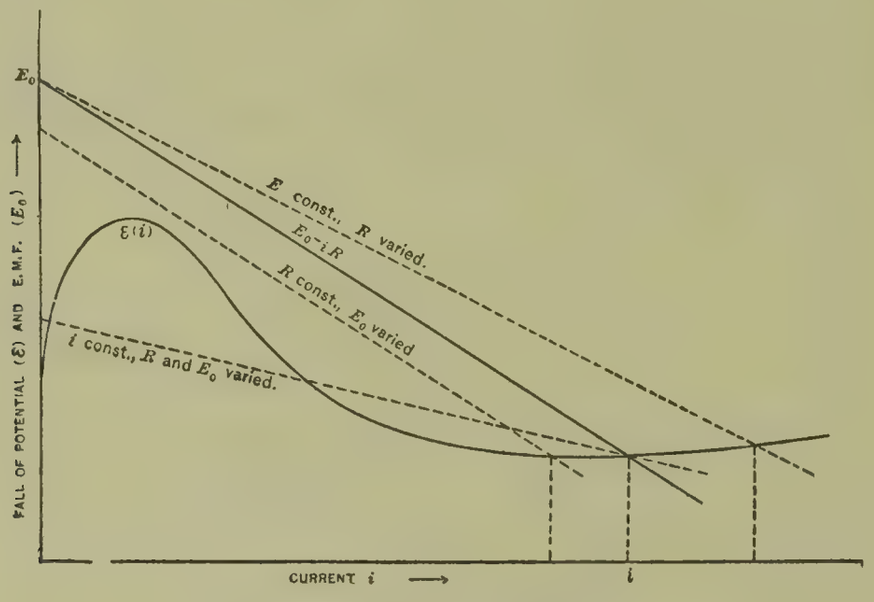

FIG. 2. Kaufman Diagram.

Suppose now an E. M. F., E_0, be applied to a gas whose characteristic at this particular pressure and section are known. Without control resistance, the current will suddenly jump from a low (brush) value to an excessively high value. With Ohmic control resistance R, the current may be determined graphically by means of the Kaufmann diagram (Fig. 2). The line E_0-iR, for any given values of E_0 and R, will intersect the gas curve E (i) at one or three points, the current being the abscissa of the point of intersection.[1]

If either the control resistance R or the E. M. F. E_0 be variable, the current may be varied from a high value down to the point where the E_0-iR line becomes tangent to the characteristic curve on its lower side. Here the current breaks, dropping to the brush discharge on the first slope of the curve. To start the heavy current again, either R must be decreased or E_0 increased until

[1] P. G. Nutting, Bureau of Standards Bulletin **1**, 403-5 (1905).

E_0-iR becomes tangent to E (i) on its *upper* side. Intermediate slopes of E_0-iR give intermittent currents and conditions for resonance. To plot a complete characteristic curve it is evidently

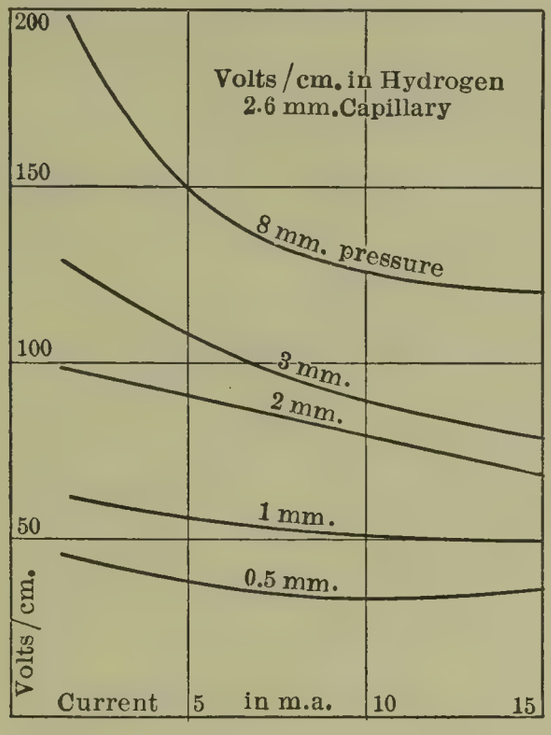

FIG. 3.

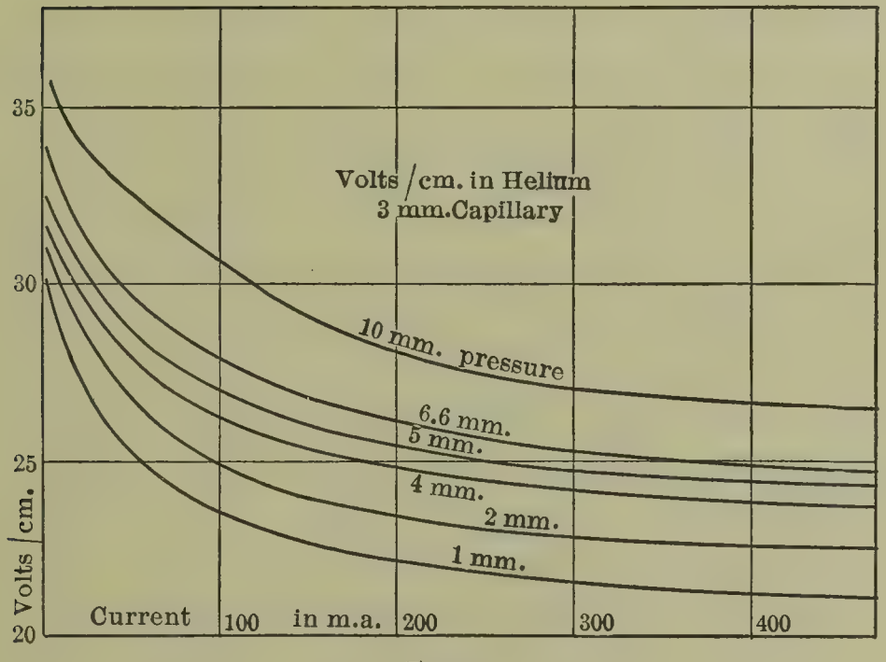

FIG. 4.

necessary to have both E_0 and R very large and one of them variable over a wide range of values.

In Figs. 3 and 4 are shown recent carefully determined data[2]

[2] Bull. Bureau of Standards, **7**, 49-70, (1910).

on gradient as a function of current in hydrogen and helium at various densities.

If we accept the kinetic theory of gases and the electron theory of electricity, the phenomena of gas conduction lead at once to the conclusion that an electric current or discharge through a gas is a convection of carriers. The number and mean velocities of these carriers determine the current, while their mobility and ease of production and recombination determine the potential gradient.

The initial portion of the characteristic curve (see Fig. 1), where gradient and current increase together, represents the condition of a current carried by *ions*—whole atoms or groups of atoms—each with an electron too few or too many for neutrality. With increased gradients or a more liberal supply of electrons the electrons move independently of the atoms and generate fresh electrons from the atoms by collision. When the characteristic curve is horizontal the electrons are increasing at a rate just sufficient to balance the decrease in mean velocity; when the slope is towards the right, the production of electrons is still more rapid.

The initial rising part of the curve is extremely steep unless there is a supply of ions aside from those produced by impact. In flames and near plates or wires heated to a high temperature or exposed to ultra violet light, there is such a supply and the initial straight portion of the curve may slope at a considerable angle. The straight portion breaks where electrons begin to move independently of the atoms and produce other electrons by impact.

Recent advances in gas conduction relate largely to the theory of ionization. The energy required to tear an electron from an atom has been determined by many observers[3] using various methods. This energy is between 1 and 2×10^{-11} erg. The theoretical value of the work required to remove an electron from the surface of an atom to infinity is $e^2/\gamma = (3.4 \times 10^{-10})^2/10^{-8} = 1.16 \times 10^{-11}$ erg. To remove one electron from each atom in a mass of gas at this rate would require for air about 12,000 calories per gram, or roughly twenty times that required to vaporize water.

The core of the theory of gas conductivity is the relation

[3] For review, see Kleeman, Proc. Roy. Soc., June, 1910.

between gradient and current. We write $i = n\,e\,u$, both n and u being functions of gradient X. The difficulty is to determine $n(X)$. Dr. Bergen Davis[4] has developed a theory of impact, which has been well substantiated by experiment. He makes the simple assumption that ionization will occur when the normal component of the impact exceeds a certain minimum value. His theory may be developed as follows:

Out of p paths taken at random in a gas

$$dp = \frac{p}{\lambda_m}\, e^{-\lambda/\lambda_m}\, d\lambda$$

have lengths between λ and $\lambda + d\lambda$.

Of the p paths $\qquad (\rho = \lambda_c/\lambda_m)$

$$p_i = p/\lambda_m \int_o^\infty e^{-\frac{\lambda_c + x}{\lambda_m}} \frac{x}{\lambda_c + x}\, d\lambda \qquad \left(E(\rho) = \int_\infty^\rho \frac{e^{-u}\, du}{u}\right)$$

$$= p\,(e^{-\rho} + \rho E(\rho)) = pI \qquad \left(u = \frac{\lambda_c + x}{\lambda_m}\right)$$

have a normal component $> \lambda_c$.

The validity of this formula was tested by Davis on his own and on Townsend's data, and just recently by Bishop[5] over a range of pressure from 1 to 40 cm. in H_2 and 1 to 5 cm. in air and CO_2. There is no systematic departure from the law.

Hydrogen		Carbon Dioxide		Air	
Pressure in cm.	$X\lambda_0$	Pressure in cm.	$X\lambda_0$	Pressure in cm.	$X\lambda_0$
1	9.67	1	6.44	2.64	10.20
1.9	9.59	3.53	6.28	4.92	10.22
4	9.64	5	6.17	5.27	10.18
5	9.68	6.05	6.16	10	10.22
10	9.72	10	6.21		
20	9.68				
30	9.67				
40	9.64				

[4] Bergen Davis, Ph. Rev. **24**, 93-102 (1907).

[5] E. S. Bishop, Ph. Rev. November 1911.

The critical paths and energies are:

	$X\lambda_c$	$Xe\lambda_c$
H_2	9.66 volts	1.58×10^{-11} erg.
CO_2	6.21 "	1.01 "
Air	10.21 "	1.67 "

Consider now the four kinds of simple impacts[6] preceding the occurrence of multiple ionization and ionization by positive ions. Of p paths:

1. $p_i = pI(N-n)/N$ gives new electrons $\rightarrow(\pm)\ (+)\rightleftarrows$
2. $(p_i) = pIn/N$ gives no net change $\rightarrow(+)\ (+)\rightarrow$
3. $p_r = p(1-I)n/N$ results in recombination $\rightarrow(+)\ (\pm)\rightarrow$
4. $(p_r) = p(1-I)(N-n)/N$ gives no net change $\rightarrow(\pm)\ (\pm)\rightarrow$

In the steady state the fresh ionization is just balanced by recombination, hence

$$p_i = p_r$$

$$\frac{n}{N} = I$$

In other words, the percentage ionization in the steady state is equal to the percentage of neutral collisions resulting in ionization.

This theory may be extended by considering impacts resulting in 2, 3, 4, or more electrons. It may be noted that there is considerable overlapping, *e. g.*, some collisions resulting in two or more electrons while others are still giving but one.

The energy changes in gas conduction are relatively very great. The rate of supply $X\,i$ represents energy used in accelerating the carriers. The bulk of the energy loss must occur during collisions of electrons with either atoms or positive ions, the result being a sudden loss of considerable energy as a wave train. According to modern views each wave train contains a definite quantity of energy proportional to the frequency.

In Figs. 5 and 6 are shown how the relative values of various

[6] P. G. Nutting, Astroph. J. **31**, 74 (1910).

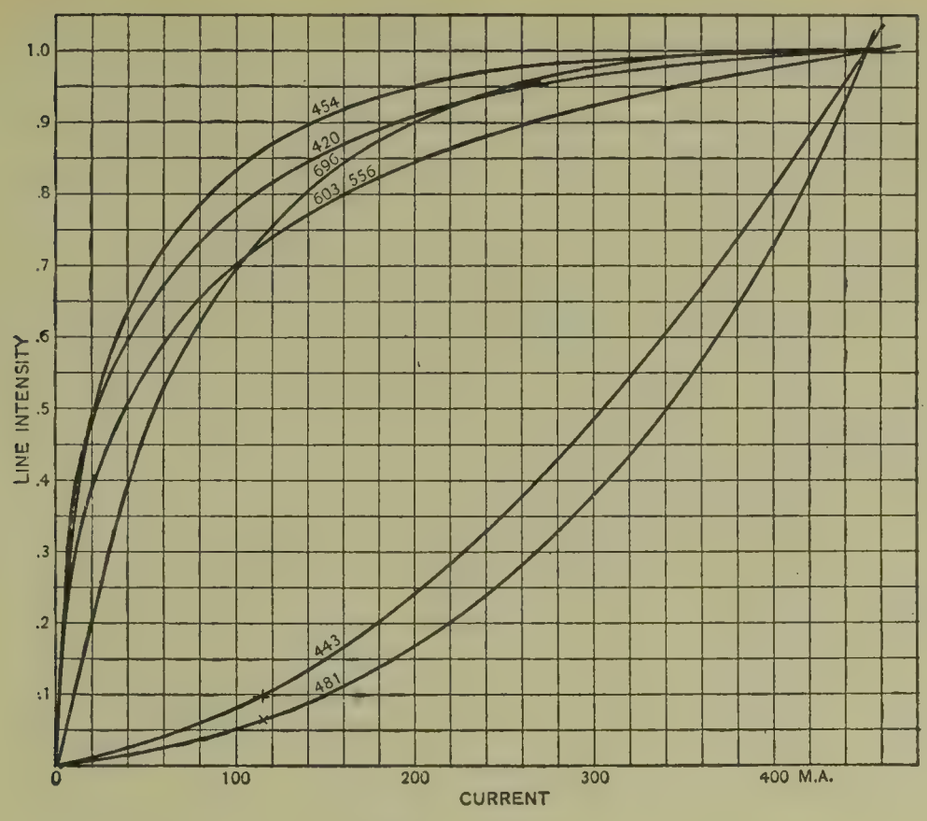

FIG. 5. Argon.

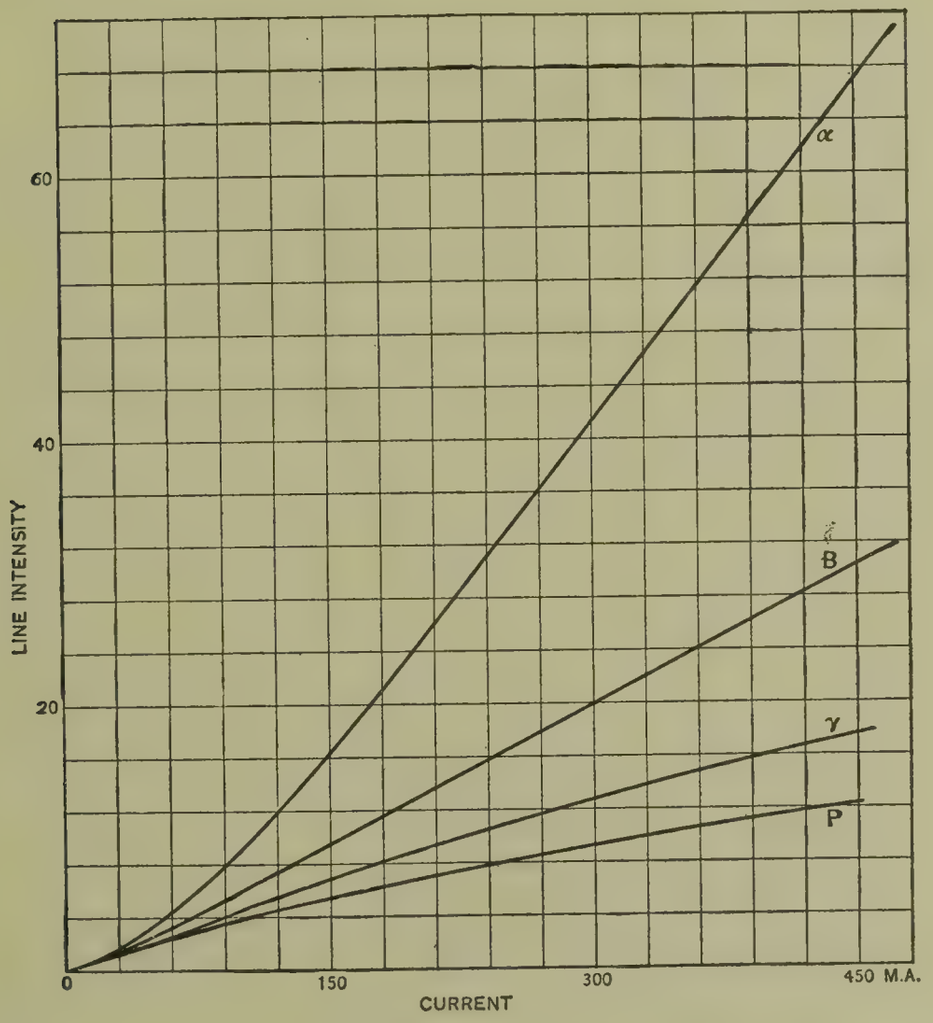

FIG. 6. Hydrogen.

kinds of energy losses vary with current density[7] in hydrogen and argon.

The radiation of the whole atoms is roughly proportioned to n and hence to i, while the radiation from the positive ions is roughly proportioned to n^2 or to i^2. Hence we conclude that primary spectra come from whole atoms, secondary from positive ions. The absence of secondary spectra in helium and neon would thus accord with low energy losses and the high conductivity observed.

[7] Bull. Bureau of Standards, **7**, 49-70 (1910).

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

GASEOUS IONS AND CHEMICAL ACTIVITY.

By S. C. Lind.
(Department of Physical Chemistry, University of Michigan.)

Although we recognize that there is a close relation between electrolytic conduction and chemical action, and although we ascribe unusual chemical activity to the free ions in electrolytes, it appears to be the consensus of opinion that there is no corresponding electrochemical equivalence in chemical reactions produced in gases by electrical conduction. This view is supported by the repeated observation that Faraday's Laws do not apply, the observed chemical effect in gases is usually largely in excess of the electrochemical equivalent of the current.

It is the purpose of the present paper to attempt to show that recent radioactive evidence indicates the existence of an electrochemical equivalence in gas reactions, quite as strict as in electrolysis, but in a somewhat different sense. It is only necessary to direct the attention to the discharge of ions rather than to the passage of current. The two are identical in electrolytic conduction, because there is no permanent discharge of ions except at the electrodes, which results in the passage of current and the production of an equivalent amount of chemical reaction.

The discharge of ions in gases, on the other hand, may take place in two ways: at the electrode, and throughout the gas by a process of recombination. It is, of course, only discharge at the electrode that produces passage of current. If discharge by recombination can also result in chemical action, evidently the latter bears no direct relation to the passage of current. In other words, there is no reason to think Faraday's Law in its ordinary form should hold and the demonstration that it does not, is in no sense a proof that chemical equivalence does not hold for the immediate reaction produced by the discharge of ions.

A limiting case of great importance is presented by a gas sys-

tem in which ions are being produced and recombine without the passage of any current. Such a case is represented by ionization by a radio-active source, and the quantitative examination of the chemical reactions produced in such a system presents great theoretical interest and has an intimate connection with our present subject. There are three general possibilities with respect to such reaction. It might prove to be less than the ionic equivalent would require, indicating a recombination of the ions to form the original gas from which they were generated; this case would throw no light on the question of equivalence. In the second case, the reaction might prove to be *in excess* of the ionic equivalent, which would indicate a catalytic effect of the radiation, which one would expect to be confined mainly to reactions proceeding in the direction of the consumption of the free chemical energy. This case would also offer no support to the idea of equivalence, and might be regarded as rather strong evidence against it. The third case, that of *equality* between the number of ions and the number of molecules reacting, is the one which has been found by the author actually to hold for practically all of the gas reactions that have been examined.

In a preliminary report to the American Chemical Society at its meeting in December, 1911, the author showed that for about a dozen different reactions of very varied chemical nature, which include all the present available data on the subject, a close agreement exists between the number of ions produced in a gas by the α particles, and the number of molecules or other chemical equivalents entering into reaction. This must be regarded as the more striking when it is considered that one is dealing with two sets of values of the order of 10^{18} to 10^{21} which might have been found to vary independently of each other through any ratio whatsoever. It is certainly notable that the ions in so many cases recombine almost quantitatively to form new products, and not the original gases.

It should be mentioned that the mere approximate equivalence of ions and molecules does not prove that the reactions may not result simply from a bombardment by α particles, because the number of ions formed is also of the same order as the number of molecular impacts. It is not possible with the present data to decide between a mechanical and an ionic theory; they might

prove to be essentially identical. A bombardment theory apparently suits reactions of decomposition quite well, but seems to be wholly inadequate for reactions of combination. The fact that reactions proceeding in the direction of the chemical free energy also obey the same law of electrochemical equivalence, is in favor of an ionic mechanism.

Quite aside from any theory, it appears that it requires the expenditure of the same quantity of kinetic energy to make molecules react, whether in the same sense or in a sense opposed to the energy of the reaction itself. This is a decidedly novel idea in chemical kinetics, which seems to present many interesting possibilities in gas reactions, but its further discussion would lead too far from the present subject.

The radio-active evidence is seen, then, to be in favor of a strict chemical equivalence where ions are being discharged by recombination to form new chemical products. Admitting that this is so, can it be explained from our present knowledge of gaseous ions? One of the most fundamental properties of gaseous ions, and perhaps also of electrolytic ions, is their attractive power on the surrounding molecules. Velocity measurements have shown that the ions in air at atmospheric pressure consist of single charges associated with about twenty to thirty molecules of oxygen or nitrogen. Suppose that such a charged molecular aggregate comes into contact with an opposite charge, or perhaps an oppositely charged aggregate; electrical neutrality is established, and the centers of attraction having been removed, the aggregate undergoes a dissociation, which may stop, however, under favorable conditions of temperature, at a polymer higher than the ordinary one, or, at least, an equilibrium will be established. Such a process would account for ozone formation in oxygen, and may also explain the active forms of nitrogen and of hydrogen that have been found by Strutt[1] and Langmuir[2] to be obtainable at low temperature, in conjunction with electrical discharge in nitrogen, and under conditions that were at least favorable to the formation of therm-ions, in the case of hydrogen.

In a mixture of two or more gases, or in gases that are not elemental, it does not appear to be so simple to form a satisfac-

[1] Strutt, Proc. Roy. Soc. **85**, 219.
[2] Langmuir, Tr. Amer. Electrochem. Soc. **20**, 225 (1911).

tory hypothesis on an ionic basis which will explain the reactions observed. For example, it is not evident how to explain on the same hypothesis the formation of HBr from its elements and its decomposition into the elements under radioactive action, although ionic equivalence holds approximately in both cases. In general, it should be stated that the experimental data are hardly of such a nature as to permit of the choice of exact mechanisms for the radio-actively produced reactions; and, in fact, it may never be possible to choose definite mechanisms, because the variety of gaseous ions is far greater than we are accustomed to deal with in electrolysis. This presents far more possibilities in the first place, and the fact that the reactions of gas ions take place under high dilution favors the procedure of two or more reactions simultaneously, thus introducing further complications.

At present we content ourselves with reiterating that in a number of gas reactions the ratio of ions to molecules is approximately equal to unity. Of course, it is not meant to predict that this will prove to be true for every gas system; there appears to be no reason to think that ions may not recombine in the same way that they were formed, without leaving any resultant chemical action. The two limiting cases would be represented by ionic efficiency of zero and of one hundred percent, and any values, whatsoever, between these, might occur without invalidating the theory in the least.

On the other hand, would it be possible for reaction to be produced in excess of the ionic theory without its invalidation? The only case of this kind which has presented itself as far as radioactive influences are concerned, is the combination of hydrogen and chlorine gases, which has been reported as taking place to an extent far in excess of the probable ionization. I say the *probable* ionization, because it has never been determined directly for elemental chlorine, but it is not likely that it is abnormal to an extent that would be sufficient to bring the reaction into accord with the ionic theory. The only other alternative would be the assumption of an auto-ionization, taking place at the moment of chemical action between hydrogen and chlorine. For many reasons this does not appear so improbable as one might be inclined to believe, among others may be mentioned the abnormal photochemical activity of chlorine.

The production of ions or electrons by chemical action is becoming rapidly more widely recognized. In the second edition of "The Conduction of Electricity Through Gases," Sir J. J. Thomson[3] devotes a chapter to its consideration, though most of the cases with which he deals are not strictly chemical in nature. Perhaps the best known example is the ionization produced by the oxidation of phosphorus. It has also been shown that electrons are liberated during the explosive combination of hydrogen and oxygen[4] at about one-tenth atmospheric pressure; the number was, however, about 10^7 less than required by electrochemical equivalence. More recently it has been shown by Haber and Just[5] and also by Reboul[6] that electrons and some ions are liberated by the action of various gases on the alkali metals at very low pressure. In reactions involving high amounts of chemical energy, Haber and Just find that the electrons are liberated with considerable initial velocity and the residual metal takes on a positive charge. In less vigorous reactions it is necessary to impart a negative charge in order to remove the electrons. The quantities in these cases approach within about 10^3 of chemical equivalence. Haber and Just also regard it as wholly possible that electrons are liberated during reactions between gases, though they have not undertaken the experimental demonstration, which involves rather great difficulties.

A theory of auto-ionization to explain abnormal effects in dealing with some of the problems of gas kinetics seems to offer many advantages over the present ones, but is still beset with so many difficulties, both experimental as well as theoretical, that a further consideration of it in this connection would hardly appear justified.

Let us finally examine the direct evidence in regard to an electrochemical equivalence in reactions produced by the passage of electricity through gases at ordinary pressure, in the form of silent or spark discharges. A typical case is met in the extended investigations of Warburg[7] on the electrical production of ozone, at the conclusion of which he finds that Faraday's Law does not

[3] Conduction Electricity Through Gases, 2d Ed., Chap. 14.
[4] Haselfoot and Kirkby, Phil. Mag. **8**, 471 (1904).
[5] Haber and Just, Ann. d. Phusik, **36**, 308 (1911).
[6] Reboul, Radium **8**, 376 (1911); Compt. rend. **149**, 110 (1909).
[7] Warburg, Berlin Akad. 1904 *et seq.*

apply; the quantity of ozone obtained was several hundred times in excess of the current equivalent, and he concludes that the production of ozone is an effect of ultra-violet light. Of course we know that ultra-violet light and ozonization are frequently produced simultaneously, but so is ionization also; and it appears that more direct quantitative evidence is needed to settle this question than is now at hand. The author feels that he is not so competent to pass judgment on this matter as some of the other gentlemen taking part in this symposium, but nevertheless will venture the opinion that under the conditions of voltage and electrode distances employed by Warburg, there may well have been a production of two to three hundred ions by collision for each electron reaching the electrode, and that the former were instrumental in the ozone formation but played no part in conduction. Such a view is certainly supported indirectly by the experiments of the author[8] on ozone formation by α particles, in which it appeared that one pair of ions is involved in the production of each molecule of ozone. If such a theory is applicable to the results of Warburg, we have a striking illustration that it is not the current that passes, but *that which does not pass,* if you will allow the expression, that produces the chemical effect; or we have a kind of inverted form of Faraday's Law.

The question may also be raised whether the ions which are discharged at the electrodes may not also undergo the same chemical reaction as those that recombine. This is a matter for experimental determination that seems to have little important theoretical bearing. Evidently in the case of ozone formation by spark or silent discharge, it would make no difference in the output, since the discharge at the electrode appears negligibly small compared with the total.

It is quite clear, then, that there must be an inherent uncertainty in dealing theoretically with gas reactions brought about by high voltage discharges at ordinary pressures, as to what fraction of the ions formed reaches the electrode. Increase of the voltage imposed brings up more ions, but at the same time increases the velocity of the electrons, which in turn largely augments the number of ions by shock. It is on account of these unavoidable factors of uncertainty in dealing with ionization

[8] Lind, Sitzungsb. d. Wiener Akad. Dec. 1911; Amer. Chem. Journ. **47**, 397.

produced electrically, that the author is inclined to regard the indirect radio-active evidence as particularly instructive regarding the electrochemical nature of gas reactions. In fact, radium furnishes a very advantageous source of ionization for such investigation, but it is an unfortunate feature that rather large quantities of radium are required to produce measurable chemical effects.

A brief summary may be given of the reasons for believing that reactions produced in gases by electrical and radio-active agencies are ionic and not atomic in nature.

(1) Gaseous ions possess a well-known power of attraction through which a number of molecules are collected around an ionic or electronic center, which process might be called "electrical polymerization."

(2) On removal of the center of attraction by electrical neutralization, a process of depolymerization or dissociation takes place, which may result in a quantitative production of a lower polymer, which is, nevertheless, higher than the elemental gas itself, and is endowed with unusual chemical activity. Ozone formation illustrates such a process. (Active forms of nitrogen and hydrogen as well as a yet higher polymer of oxygen, O_5, have also been obtained through electrical influences.)

(3) In all chemical actions brought about through the agency of α particles, either in gaseous or liquid systems, there is a notable equivalence between the number of ions and the number of reacting molecules.

(4) From analogy with electrolytic ions, great chemical activity as well as electrochemical equivalence in reaction, might also be expected in the case of gaseous ions.

(5) Evidence in regard to atomic activity is mainly negative. We really know very little about the atoms of the diatomic or polyatomic gases. The supposed "nascent activity of the atoms" may be purely a myth. Our knowledge of the monatomic gases, such as argon, certainly indicates anything but chemical activity. Nor is mercury vapor particularly active ordinarily, but seems to be so immediately after the current is stopped in a mercury-arc lamp. In short, it appears that there is no real experimental

evidence to support the view of abnormal activity of the atoms, while there is every reason to believe that ions are frequently if not always chemically active.

Chemical Laboratory of the University of Michigan,
Ann Arbor, April 13, 1912.

A paper presented in the Symposium on Electric Conduction, at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

THE OIL-DROP METHOD OF STUDYING ELECTRICAL PHENOMENA IN GASES.

By R. A. Millikan,
(Professor of Physics, University of Chicago).

Two years ago I had the privilege of presenting at the meeting of the American Electrochemical Society in Chicago preliminary results obtained by what we may call "the oil-drop method" of studying electrical phenomena in gases.

These results may be very briefly summarized as follows: (1) That study furnished, perhaps, the most direct and most irrefutable proof that has yet been brought forward of the granular or atomic structure of all electrical charges. (2) It made it possible to determine with a high degree of accuracy the absolute value of the elementary electrical charge. (3) It made it possible to demonstrate that the positive ion and the negative ion in gases are absolutely alike so far as electrical charge is concerned. (4) Since it had long before been shown that electrical currents are nothing but electrical charges in motion, it furnished most convincing evidence that an electrical current is simply the motion of definite elements or atoms of electricity (whatever electricity may be) through or over the conducting material.

I have been asked by the president of our Society to present today what further results have been obtained in the use of this method of studying electrical phenomena in gases, and I will first summarize these results very briefly as follows:

First: We have been able to demonstrate, I think, that the process of ionization in gases—under all the conditions which we have been able to study, by X-rays and by the *beta* and *gamma* rays of radium—consists in the detachment of one single electron from each ionized molecule; in other words, that the phenomena of valency shown in electrolytes do not appear in

gaseous ionization, insofar as we have been able to obtain ionization with the ordinary agents. Of course it is entirely possible that there are agencies or conditions not yet studied which do produce poly-valent ions in gases, but we have found no evidence thus far in favor of this conclusion.

Second: We have been able to do one of two things, namely, either to bring forward complete proof of the absolute identity of the charge of the gaseous ion and that of the univalent ion in electrolysis, or to bring forward the complete quantitative proof of the correctness of the kinetic theory of Brownian movements. I like to look at it from the latter point of view, because I think that the former contention has been sufficiently well established by preceding experiments. Our success in bringing forward this proof has been due to the fact that we have been able to eliminate completely that unknown resistance factor of the medium which stood in the way of all preceding attempts in this direction.

Third: We have been able to determine this resistance factor of the medium and thus to find the law of fall of a drop through air at all pressures, from one atmosphere down to one-fiftieth atmosphere. This is of importance to the subject of electrical conduction only because it makes possible a high degree of precision in the evaulation of the elementary electrical charge.

Fourth: In view of this fact we have redetermined within the past year all of the factors which enter into the evaluation of the elementary electrical charge, so that I think it is not too much to say that we now know it with an accuracy of from one-fifth to one-tenth of one percent.

Fifth: The oil-drop method has enabled us to obtain some new and interesting information about the relative mobilities of positive and negative ions in strong fields.

I will very briefly outline the way in which these results have been obtained, but, for the sake of making the transition from the older to the newer experiments, let me first review the general method.

When the terminals of the 10,000-volt battery, *B*, are thrown upon the plates, *M N*, of an air condenser (Fig. 1), it is found that the gas between the plates remains absolutely stagnant, no convection currents of any kind being set up. This shows that

the molecules of the air between the plates must be completely neutral, *i. e.*, if they possess electrical constituents at all, then they must contain positive and negative electricities in exactly equal amount. If now we pass a beam of X-rays through the air between the plates, we find that the molecules are broken up by the X-rays into electrically charged fragments which shoot one toward the upper and the other toward the lower plate. This shows that the molecules of air do possess positive and

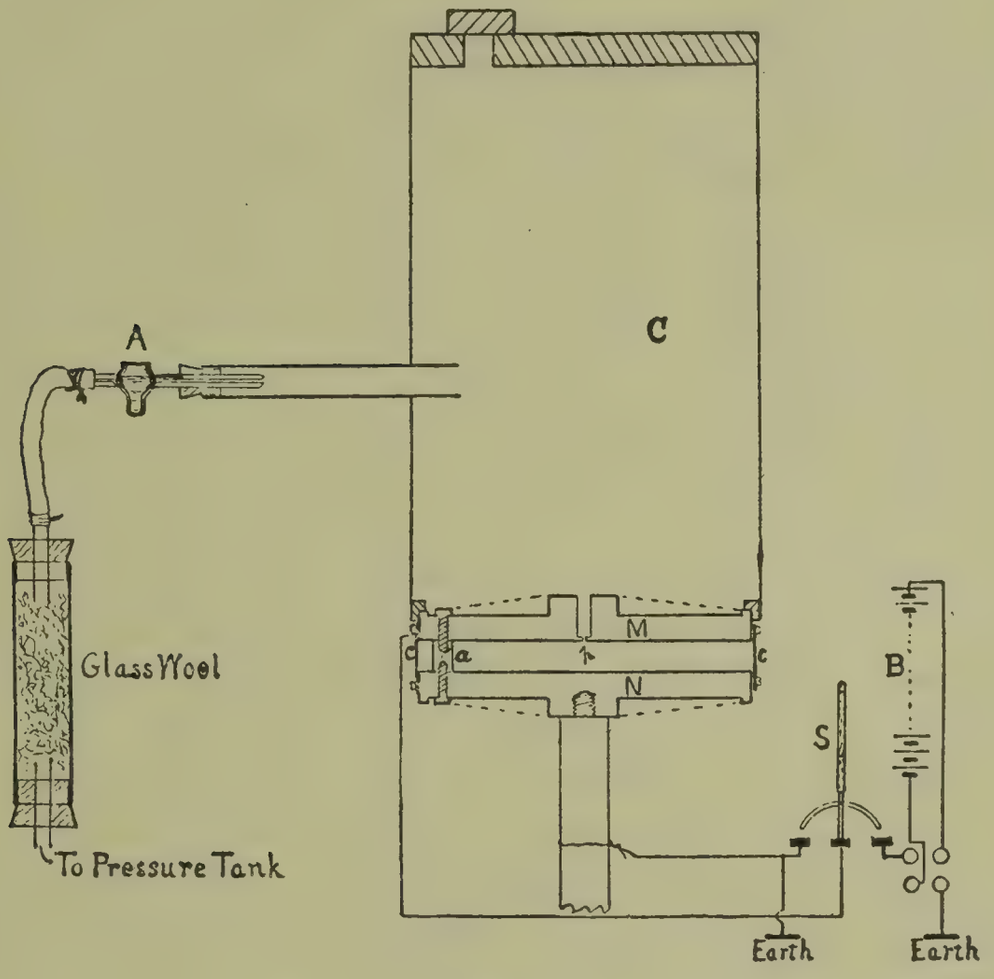

FIG. 1.

negative electrical constituents which we are able to separate by the X-rays. This process of separating the neutral air molecules into electrically charged parts we call the process of ionizing the gas, and the mechanism of ionization presumably consists in the detachment from a neutral molecule of one single negative element or electron, thus leaving the original molecule positively charged. The detached electron presumably soon attaches itself to another neutral molecule, so that the net result of the ionization is merely that two neutral molecules have been changed into

two electrically charged molecules of opposite sign. Even when there is no ionizing agent whatever present, it is found that out of the 27 billion billion molecules in 1 c.c. of ordinary air, from 2 to 20 split up per second into ions(probably because of the presence of traces of radio-active substances in the atmosphere), so that these so-called atmospheric ions exist in small numbers in all air, and it is to their existence that are due all the phenomena of atmospheric electricity which have been the objects of man's awe and worship throughout all ages. Now, the problem originally set as the object of this investigation was to catch a single one of these atmospheric ions and to measure its charge. This was accomplished with the aid of a small oil drop which was blown with an atomizer, *A*, into the space, *C*, about *M* and *N*, and then allowed to fall through the pin hole, *p*, into the space between *M* and *N*, when by alternately throwing on and off the field it was kept pacing its beat up and down in the hope that it would catch and hold fast some unwary ion which came within reach. (That the oil drop can be pulled up by the field is due to the fact that it is always charged in the atomizing process.) One never has to wait more than a minute or two before an ion is caught, the fact of the capture and the instant at which it takes place being signalled to the observer by the change in the speed of the drop in the field. Thus, if a positive drop catches a positive ion the speed is increased, while if a positive drop catches a negative ion the speed is decreased.

A drop would often be kept traveling back and forth in the manner described for four or five hours at a time, in the course of which it would change its charge twenty or thirty times because of the capture of ions, and the value of each of these different charges can be computed. The beauty and precision of the measurements and the certainty with which the atomic theory of electricity follows from the results obtained can best be appreciated by inserting in full the record of an experiment made upon a particular drop. The column headed *G* gives the successive periods of time which the droplet required to fall between two fixed cross-hairs in the observing telescope, whose distance apart corresponded in this case to an actual fall of 0.5222 centimeter. It will be seen that these numbers are all the same within the limits of error of a stop-watch measurement. The

column marked *F* gives the successive times which the droplet required to rise under the influence of the electrical field produced by applying in this case 5,051 volts of potential difference to the plates *M* and *N*. It will be seen that after the second trip up the time changed from 12.4 to 21.8, indicating (since in this case the drop was positive) that a negative ion had been caught from the air. The next time recorded under *F*, 34.8, indicates that another negative ion has been caught. The next time, 84.5, indicates the capture of still another negative ion. This charge was held for two trips, when the speed changed back again to 34.6, showing that a positive ion had now been caught which carried precisely the same charge as the negative ion which before caused the inverse change in time, *i. e.*, that from 34.8 to 84.5.

G	*F*
13.6	12.5
13.8	12.4
13.4	21.8
13.4	34.8
13.6	84.5
13.6	85.5
13.7	34.6
13.5	34.8
13.5	16.0
13.8	34.8
13.7	34.6
13.8	21.9
13.6	
13.5	
13.4	
13.8	
13.4	
Mean 13.595	

Now, all of the successive values of the charge carried by the drop throughout the experiment can be easily computed from the constant speed under gravity and the successive values of the speed in the electric field. To find the *absolute* values of these charges it is indeed necessary to know the weight of the drop, and the determination of this weight may involve an error of 1 to 2 percent at most, but since this weight remains constant throughout the experiment the *relative* values of the successive charges can be found with absolute certainty and with great precision without any knowledge of this weight. They are, in

fact, simply proportional to the successive values assumed by the sum of the two speeds, *viz.*, that under gravity and that in the field.

In the case of bodies moving slowly and uniformly through a resistance medium any two forces produce velocities which are proportional to the forces. The downward force due to gravity is here mg, and the upward force due to the field is Fe, in which F denotes the strength of the field and e the charge on the drop. Hence, if v_1 is the downward velocity due to gravity, and v_2 the upward velocity due to the excess of the upward pull of the field over the downward pull of gravity, we have

$$\frac{v_1}{v_2} = \frac{mg}{Fe - mg} \text{ or } e = \frac{mg}{Fv_1}(v_1 + v_2) \qquad (1)$$

Similarly the charge carried by any captured ion is proportional to the *change* produced in this sum $(v_1 + v_2)$ by the capture. Now, the change in this sum produced by the capture of the ion which caused the time in column F to change from 34.8 to 84.5 was, as anyone who wishes can verify, 0.00891 cm. per sec., and the successive values of this sum arranged in order of magnitude were 0.04456, 0.05347, 0.06232, 0.07106, 0.08038. If, now, electricity is atomic in structure, all the different charges appearing in this experiment, those on the ions and those on the drop, should be exact multiples of the elementary unit of charge, which means that all of the numbers above given should be exact multiples of something. Dividing the above five numbers by 5, 6, 7, 8 and 9, respectively, gives 0.008912, 0.008911, 0.008903, 0.008883 and 0.008931, which are all seen to be within one-fifth of one percent of the value of the *change* in the sum of speeds produced by the capture of the ion which caused the numbers in the column F to change from 34.8 to 84.5. *Hence the charge carried by this ion was itself the elementary unit out of which all of the other charges which appeared in the experiment were built up.*

Nearly a thousand different drops have been examined in the manner indicated, some of them being of oil, a non-conductor, some of glycerine, a semi-conductor, some of mercury, a good conductor, and some of other substances, and in every case, without a single exception, the initial charge placed upon the

drop by the frictional process, and all of the dozen or more charges which have resulted from the capture by the drop of a larger or smaller number of ions, have been found to be exact multiples of the smallest charge caught from the air. Some of these drops have started with no charge at all, and one, two, three, four, five and six elementary charges or electrons have been picked up. Others have started with seven or eight units, others with twenty, others with fifty, others with a hundred, others with a hundred and fifty elementary units, and have picked up in each case half a dozen elementary charges on either side of the starting point, so that in all, oil drops containing every possible number of electrons between 1 and 150 have been observed and the number of electrons which each drop carried has been accurately counted. It is not found possible to count with certainty the number of electrons in a charge containing more than 200 of them, for the simple reason that the method of measurement used fails to detect the difference between 200 and 201. But it is quite inconceivable that large charges such as are dealt with in the commercial applications of electricity can be built up in an essentially different way from that in which the small charges whose electrons we are able to count are found to be. Furthermore, since it has been definitely proved that an electrical current is nothing but the motion of an electrical charge over or through a conductor, it is evident that the experiments under consideration furnish not only the most direct and convincing evidence that all electrical charges are built up out of these very units or electrons which we have been dealing with as individuals in these experiments, but that all electrical currents consist merely in the transport of these electrons through the conducting bodies.

Having thus briefly presented the method and shown some of its capabilities, I will attempt to explain in as few words as possible how the five later results mentioned above have been obtained.

I.

The proof that *the ionization of a gas molecule by X-rays or the beta or gamma rays of radium consists in the detachment from a neutral molecule of one single elementary charge* was obtained by placing a very small, positively charged drop between

the plates M and N (Fig. 2), and then adjusting the field so that the drop was just balanced, the force of gravity being exactly neutralized by the upward pull of the field. A sheet of air beneath the drop was then ionized by means of the X-rays or the radium rays in the manner shown in the figure. Under these conditions the "balanced drop" was in a veritable shower of the positive residues of the molecules split up by the rays. When one of these positive ions strikes the drop the latter instantly starts upward with a speed which can easily be measured and from which the value of the charge which was on the ion can be computed. If the act of ionization consisted in the detachment of two or more electrons from a single molecule, the positive residues would carry a corresponding number of unit charges and

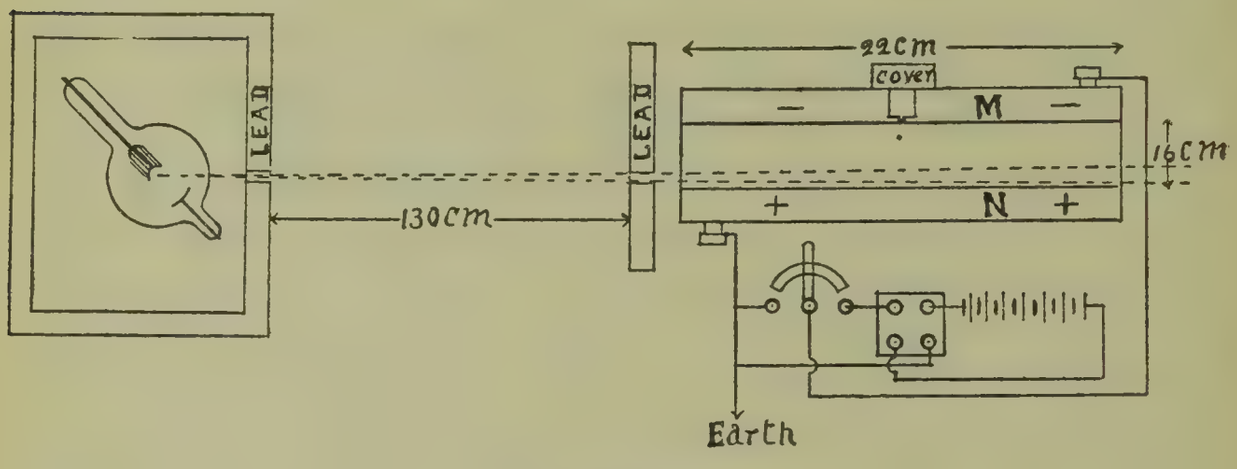

FIG. 2.

the speed of the drop after it was hit by one of these positive residues would correspond to the addition of two or more elementary units of electricity to the drop. As a matter of fact, Mr. Harvey Fletcher and myself, in the course of three months, studied some 500 "catches" of this sort, 496 of which were certainly "singles," and but four of which were in any way uncertain. Since none of these four could with certainty be attributed to the capture of positive residues carrying two or more charges, our conclusion was that we could find no evidence at all that the act of ionization of a gas molecule ever consists in the detachment of more than one electron from a neutral molecule, while in practically all the cases which we were able to study our evidence was conclusive that the act of ionization does in fact consist in the detachment of one single electron.

II.

The proof that *the charge carried by a gaseous ion is identical with that carried by a univalent ion in electrolysis, or* the proof of *the correctness of the kinetic theory of Brownian movements,* was made as follows: It had been discovered as early as 1827, by an English botanist, Brown, that microscopic particles in a liquid keep up incessantly a very minute trembling motion, and this phenomenon remained altogether unexplained for more than half a century. At last, in 1888, it was suggested by Gouy, in France, that this trembling motion was probably due to the fact that when a particle is sufficiently small the molecular bombardment which it receives from the molecules surrounding it is not at a given instant exactly the same on opposite sides, and in consequence the particle is pushed first in one direction and then in another by these unbalanced molecular forces. In 1908, Perrin, in Paris, with the aid of a formula deduced by Einstein, of Bern, brought forward quite convincing evidence that this explanation was correct, but Perrin's observations had all been made upon minute particles suspended in liquids, and liquids are very much less suited to any convincing and accurate test of the kinetic hypothesis than are gases. Apparently the very great advantages of observing minute suspended particles in a gas at very low pressures, where the motions ought to be enormously increased, had not been appreciated, or, at least, had not been utilized, perhaps because the means had not before been at hand for keeping such particles in suspension. Accordingly, the plates, *M* and *N*, shown in Fig. 1, with the atomizer attached, were placed inside a large brass cylinder, which could be sealed air-tight and exhausted if desired. When the air was at atmospheric pressure the smallest particles produced by the atomizer showed clearly the incessant wiggling motions which are called, after their discoverer in liquids, the "Brownian movements." But when the pressure was reduced to seven or eight millimeters of mercury (about 0.01 atmosphere) these motions had increased so enormously in violence that it was difficult to follow the smallest particles as they dashed hither and thither like wigglers in a water-barrel. The reason that reducing the pressure brings out the motion so much more clearly is obviously this: When the

oil-drop is surrounded by a dense swarm of bombarding molecules it is like a football in a *melée* of densely packed players who are kicking in on all sides at once, but are unable to send it any appreciable distances. But when it gets out into the open, where the players are scarce, it begins its spectacular flights. Precisely so with the oil-drops, and no football game was ever more

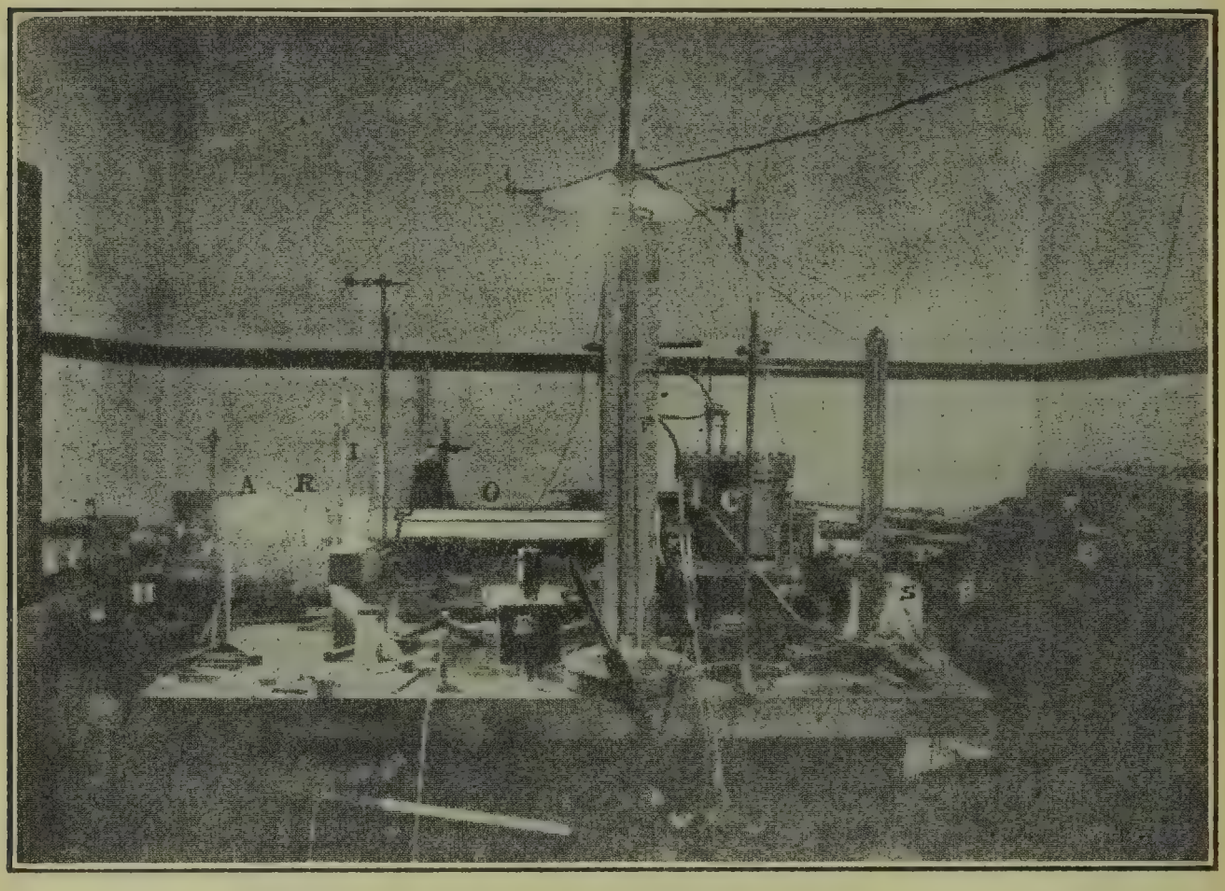

FIG. 3. Arrangement of Apparatus.

A, arc light for illuminating droplet. *H*, chronograph for measuring speeds of droplet. *R*, lens for making the beam from the arc parallel or slightly convergent. *I*, shutter for intercepting altogether the light from the arc save when a reading of a transit of an "oil star" over a cross-hair was to be taken. This was used to insure entire stagnancy of the air between the plates *M* and *N* (Fig. 7). *E*, high potential static voltmeter from measuring *PD* produced by *B*. *P*, mercury pressure gauge or manometer for measuring the pressure of the air within *C*. *C*, airtight brass chamber containing the plates *M* and *N* of Fig. 1. *W*, pressure pump for forcing a puff of air through the atomizer inside of *C* and above the plates *M* and *N*. The same pump is also used for exhausting the cylinder *C*. *T*, telescope for observing illuminated droplet. *S*, switch for throwing on or off the electric field between the plates. *B*, ten-thousand-volt storage battery. *T*, spot of light produced by the beam after passing through two windows of the chamber *C*. *Q*, opening in lead box through which X-ray beam emerges on its way to chamber *C*, where it ionizes the gas between plates *M* and *N* of Fig. 1. *X*, X-ray bulb. *O*, cylindrical glass trough 80 cm. long filled with water for absorbing the heat rays from the arc.

spectacular or more fascinating than the behavior of one of these oil-drops at low pressures. The fact that the motions increase in violence the rarer the gas becomes and the smaller the particles are taken (size being indicated by the speed with which a given

particle settles under gravity) is obviously just what ought to happen. There can not then be the slightest doubt that what these oil-drops are doing, namely, dancing about violently in all sorts of directions, is precisely what the molecules themselves are doing in a much more excited way, for it would be absurd to suppose that the increased speed and the increased distance of the motions as size and mass diminish do not go on after the particles cease to be visible and shrink to molecular dimensions. From the standpoint of a molecule, which is darting hither and thither with the speed of a rifle bullet, our dancing oil-drops must look like snails crawling about with languorous slowness. But to us they have served their purpose, for they have enabled our minds to see the invisible molecular world doing in a large way just exactly what the oil-drops are doing in their small way. They have proved the kinetic theory of matter even to the man on the streets.

But while seeing the oil drops dance may satisfy the average man, the scientist wants a rigorous, quantitative proof. This was obtained as follows: In 1905, Einstein, as indicated above, showed that if a body like one of our minute oil-drops is dancing about in a resisting medium subjected to no forces but those arising from its own energy of agitation, that is, from the bombardment of the surrounding molecules, the mean distance through which it will drift in a given time, say ten seconds, from its position at the beginning of this time can be computed in terms of three factors: (1) Its energy of agitation, (2) a resistance factor of the medium, and (3) the length of the time-interval through which the drift is observed. But this same quantity can also be easily and directly *observed* in our experiment by simply balancing the force of gravity upon the drop by the force of an electrical field in the manner already described, and then noting over how large a distance *on the average* it wiggles in a given time by virtue of its energy of agitation. In the actual experiments, we took, in the case of each drop, the mean of several hundred observations on the distance moved in ten seconds in a vertical direction, over a set of horizontal scale divisions placed in the eye-piece of the observing telescope, for Einstein's theory was developed in such a way that the movements to right and left did not need to be considered.

Einstein's actual equation is

$$D^2 = \frac{4}{3}\frac{E}{K}t \qquad (2)$$

in which D^2 is a quantity obtained by squaring each individual displacement and then taking the mean of these squares; E is the mean kinetic energy of agitation of the drop, K is a resistance factor depending upon both the medium and the drop, and t is the length of the time interval used. If the *average* displacement, D, is used instead of the average square of the displacements, the correct form of the equation is.

$$D = \sqrt{\frac{8}{3\pi}\frac{E}{K}}\,t \qquad (3)$$

We can remove the kinetic energy of agitation, E, of the oil-drop from this equation by reflecting that, according to the Maxwell-Boltzmann law, this is the same for the oil-drop as for a single molecule, and hence is given by the familiar kinetic theory equation

$$E = \frac{3}{2}\frac{RT}{N} \qquad (4)$$

in which T is absolute temperature, R the well-known universal gas constant, and N the number of molecules in a gram molecule, *i. e.*, in two grams of hydrogen. When this value of E is substituted in equation (3) the latter becomes

$$D = \sqrt{\frac{4}{\pi}\frac{RT}{NK}} \qquad (5)$$

Now, the essential advantage in the present method of work lies in the possibility of eliminating the factor K. That this can be done is obvious from the fact that the resistance which the medium offers to the motion of a given drop through it at a given speed is, of course, the same whether it is an electrical force, a gravitational force, or a force arising from the molecular bombardment which is causing the motion. Consequently, all

that was necessary for us to do in order to eliminate this resistance factor entirely was first to observe the successive displacements of the *balanced* drop as indicated above and then to destroy the balance and measure how fast the drop moved on the average, both under gravity and under an electrical field of known strength, in precisely the way we had done when we were determining the successive values of the charge carried by the oil-drops. From the results of the two experiments we could then eliminate the resistance factor and obtain the average displacement in terms of quantities every one of which was measurable with the greatest precision.

Thus when the drop is moving down through the medium under the force of gravity, mg, alone, its average velocity, v_1, is given by $mg = Kv_1$. The substitution of this value of mg/v_1 in equation (1), p. 190, give $e = K/F\ (v_1 + v_2)$, and the elimination of K between this and (4) gives

$$D = \sqrt{\frac{4}{\pi} \frac{RT\ (v_1 + v_2)}{F\ (Ne)}\ t} \qquad (6)$$

Since D was, of course, different for different drops, instead of making the comparison between the observed and calculated values of D, it was thought preferable to make the comparison in every case between the value of Ne obtained from this equation and these experiments and the value of Ne obtained from experiments in electrolysis, for Ne is merely the amount of electricity required to separate by electrolysis one gram equivalent of any substance from a solution. The value of $\sqrt{Ne}$ obtained from the most accurate experiments on the electrolysis of silver is $1{,}702 \times 10^7$ electrostatic units. The mean value of $\sqrt{Ne}$ obtained from 1,735 displacement measurements upon nine different drops was $1{,}698 \times 10^7$ electrostatic units.[1] This agreement to within less than one-fourth of one percent between the observed value of $\sqrt{Ne}$ and that obtained from experiments in

[1] All of these computations relating to the Brownian movements were carried out most skillfully by Dr. Harvey Fletcher. It should be added, too, that in only a portion of the experiments was the observed value of the displacement obtained in precisely the manner indicated above, for it was found that greater accuracy could be obtained in the measurement of this displacement by a slight modification of the method. To make this modification applicable, however, a considerable amount of new and important theoretical work had to be done. This work was most ably and successfully carried out by Dr. Fletcher, and can be found in the August number of the *Physical Review*, 1911.

electrolysis may be taken as proving that e on the gas ion is the same as the e on the univalent ion in electrolysis, provided the kinetic theory of Brownian movements is assumed to be correct, or, if the identity of the two e's can be regarded as established by the experiments of Townsend and others, then, as indicated above, our experiments would establish the correctness of the kinetic theory of Brownian movements.

III.

The determination of *the law of fall of a drop through air at reduced pressures* is of as much theoretical interest as any other portion of this investigation, but it has a bearing upon the problems of electrical conduction only because it is one of the elements which enters into the absolute evaluation of the charge of the electron. The details of this study will be presented fully elsewhere. It is sufficient for our present purpose to state that a modified Stokes' law[2] of the form which I originally proposed, namely,

$$X = 6\pi\mu a v \,(1 + A\, l/a)^{-1} \qquad (7)$$

is found to hold accurate for drops of the size a = 0.0002 cm., at all pressures down to 6 cm. of mercury, or more generally this law is found to hold under all circumstances so long as l/a is less than 0.5, and the value of A for oil-drops in air is found to be 0.847 instead of 0.817, the value given in my original paper. For values of l/a greater than 0.5 a law of the form (7) is no longer applicable and higher order terms in l/a must be introduced to represent the phenomena. No theory which covers this behavior has yet been put forth.

IV.

In addition to the constant A of the last equation, all the other constants entering into *the absolute evaluation of e,* in particular

[2] X is the force acting upon the drop, v its velocity, a its radius, l the mean free path of the gas molecule, μ the coefficient of viscosity of the gas and A a constant which I originally determined experimentally and for which I obtained the value 0.817.

the coefficient of viscosity of air, have been redetermined with all possible precision, and the value of e obtainable from this data should involve an error of not more than 0.1 or 0.2 percent. The final averaging has not yet been completed, but it may now be said that the value of e will differ from 4.80×10^{-10} electrostatic units by but a fraction of a percent.

V.

In discussions of *the mobilities of ions in gases,* it is generally assumed that the energy which an ion possesses at the end of a free path when it is moving in an electric field is the energy taken from the field since its last impact. If this were true it would be possible to find the absolute value of the mean free path of either a positive or negative ion by the oil-drop method, by simply loading up a given drop with electricity until a field of given strength was just unable to force an ion of its own sign upon the drop. I attempted to determine mean free paths by this method to see whether the observed and theoretical values would agree. Since, in the field used, the negative ion was almost certainly an electron, while the positive ion was a body of molecular dimensions, it was to be assumed that the mean free path of the positive ion would be very much less than that of the negative ion—in fact, about one-sixth as large. Hence it was to be expected that a given field would be able to force negative ions upon a given drop when strongly negatively charged very much more easily than it could force positive ions upon the same drop when carrying an equal positive charge. Precisely the opposite was found to be the case. *Positive ions could be forced upon positive drops considerably more easily than could negative ions upon negative drops. The observed and computed values were of the right order of magnitude in the case of the negative ion, provided the latter were assumed to be an electron, but field strengths of one-tenth the values computed as just sufficient to enable given positive drops to force away positive ions were still found to force the ions into the drops.* This means merely that the assumption underlying the computation is erroneous in the case of the positive ion when the field strengths are of the sort here employed, namely, from 200 to 5,000 volts per cm. Under

such conditions the positive ion must plow its way through the gas with a velocity very much greater than the mean velocity which it would acquire between impacts. A further report upon the mobilities of both positive and negative ions in strong fields will soon be made.

A Discussion following the Symposium on Electric Conduction at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., Friday, April 19, 1912, President W. R. Whitney in the Chair.

DISCUSSION ON ELECTRIC CONDUCTION.

PRESIDENT WHITNEY: I promised at the beginning of the symposium, that we would have à discussion after the presentation of the papers, and I will give you a chance to have this discussion now. I wish, before I open the discussion, to thank heartily on my personal behalf, and on behalf of the Society, those gentlemen who have assisted in this symposium today. I am willing to assume the responsibility for any mistakes which have been pointed out, such as our failure to recognize that a fused salt is the same thing as a pure liquid, or any other mistake, because I believe that on the whole we have all profited. I will now open the subject for general discussion.

DR. E. WEINTRAUB: I wish to state more precisely my attitude toward the electronic theory of conduction in solids.

The remarkable work that has been done on the conduction of gases in the last decade has led to the assumption that in gases the current-carriers are mainly negative electrons. The development of the theory there took the natural course in the sense that the theoretical assumptions were forced on the investigator by experimental results.

The attempt to apply these results to the conduction in solids was natural and undoubtedly ought to be continued to see how far we can get. In doing so we must not, however, force the facts to fit the theory, for fear that instead of benefiting by the theory we will actually be harmed by it. To make some simple assumptions and see how far we can get with them may be useful in the beginning, but to imagine that nature must follow those simple assumptions and try to explain away the obvious discrepancies has done so much harm in the history of science that it would, perhaps, be best to learn by previous experience and not repeat the error.

The idea that the conduction in metals is due to a convection

current of charged particles is an old one and already Wilhelm Weber wrote on the subject. He and the men who took up this idea in recent times (Riecke and Drude) assumed that both positively and negatively charged particles were carriers of the current. As this led to difficulties in the explanation of the absence of transfer of matter at the contact of two metals the theory was simplified by Lorentz, J. J. Thomson, and others, to the effect that only negatively charged particles carry current. With this assumption, however, it is difficult to explain the fact that the Hall effect has opposite sign in different metals, and many other things.

Difficulties of that nature usually appear when a theory, developed on the basis of experimental evidence in one field and successful there, is transferred to a new and remote field. I was, therefore, not at all disappointed when I found that the same happened here.

The only quantitative agreement between theory and experiment in the case of the conduction in solids is found in the numerical value of the ratio of thermal conductivity to electrical conductivity and Prof. Richardson has emphasized this in his lecture. In determining the weight to be given to this agreement we must keep in mind the following general principle. If the assumptions of a theory were made for the purpose of explaining a certain fact then naturally the agreement between fact and theory in this particular field can be given but little weight as a proof of the validity of this theory. The same is true of modifications which may be made in a theory for the distinct purpose of smoothing out a certain disagreement.

In order to explain the parallelism between thermal and electrical conductivity it was assumed by the theory that the negative electrons which are supposed to carry current also carry heat. Now this assumption was made *ad hoc*. From the kinetic theory of gases and solid substances in general there was no reason to believe that neutral molecules do not take considerable part in heat conduction. In insulators the assumption of conduction of heat by neutral molecules is, of course, absolutely necessary. After having made this assumption for the distinct purpose of explaining the parallelism between thermal and electrical conductivity in metals, even a quantitative agreement, in this particular

field, between theory and experiment would hardly be of great weight as a "proof" of the theory.

Prof. Richardson has explained that the theory leads to 6.98×10^{-6} for the ratio of thermal to electrical conductivity, a value which agrees almost exactly with reality. This exact agreement, however, is a matter of accident. The theoretical ratio was derived by very simple assumption which cannot be correct. By trying to get a better approximation Lorentz got down to the figure 4, so that the agreement becomes poorer as the theory gets more perfect. The agreement is good only for ordinary temperatures and it also does not hold for a number of metals and for alloys. Of course, it does not hold for poor conductors.

When, however, we leave this field and try to see what luck the theory has with other facts of conduction of solids we get a very discouraging result. The simplest fact of electrical conductivity, namely, that the resistance of good conductors increases proportionally to the absolute temperature and that it becomes nil near the absolute zero has found no explanation as yet in the electronic theory of solids. The theory rather leads to a proportionality of resistance to the square root of temperature.

The relation between conductivity and volume is not explained by the electronic theory. The magnetic effects, such as the Hall effect, offer great difficulties.

In conclusion I would say that the conduction in solids is bound up essentially with the constitution of the solids, and that the attempt to disregard this and build up a theory on similar lines to that of gases cannot lead very far.

PROF. O. W. RICHARDSON: Dr. Weintraub has accused me, along with the other apologists for the electronic theory of metallic conduction, of taking the standpoint of an advocate, and making all my own points, and entirely ignoring everything to be said upon the other side. No doubt there is something in it, but I do not think we are alone in that situation. Our critics are not entirely blameless in this respect.

I think his treatment of the question of the ratio of the thermal conductivity to the electrical conductivity of metals is such as to be misleading to those who are not very familiar with the question. The main point is that starting from these two assump-

tions, first of all, that electricity is carried by electrons, and secondly, that heat is carried by electrons, you get to a certain formula; you probably have not forgotten it, but I will write it again: $\frac{k}{\sigma} = 3 \frac{R^2}{e^2} \theta$. Now, Dr. Weintraub says that this factor 3 is suspicious. Well, it is true that Lorentz made a slightly different supposition, and he did not get 3 there, he got, I think, $2\frac{2}{3}$, if I remember rightly, which is not very far from 3, it is about as near 3 as most of the experimental numbers on the board would require it to be; but the point is that, provided you start with the hypotheses, first of all, that the current is carried by the electrons, and secondly, that the heat is also carried by the motion of the electrons, you may get slightly different values for this factor, but you cannot alter it much, so that if you turn to the absolute value of the ratio you will get something which is between 5 and 15, let us say, not to be too exacting, multiplied by 10^{10}, for the ratio of the two conductivities, and with the simplest assumptions, we get 7 multiplied by 10^{10} almost exactly. There is no reason apart from these considerations, so far as I can see, why nature should not have made it 7 multiplied by 1 or by 10 or by 10^{20}. I think it is very wonderful that there is such an agreement in the absolute value of this physical quantity, and it is extremely unlikely to be a chance coincidence.

With regard to many of Dr. Weintraub's deductions, I think, if we had time to thresh them out, we should find we were pretty well in accord with one another. I agree with him that, in the development of the electron theory, many things have been written that will not hold water. That is always the case in the initial stages of a new theory, and you must push it in all directions before you find where it will, and where it will not work.

I think there are one or two rather salient points that it will be difficult to account for on any other theory. First of all, you have the important fact in metallic conduction that there is no metallic transportation. How will you explain it, if you do not have the electron theory? You *must* have the same thing to carry the current in one metal as in others. Another point is that you get these electrons coming out of the metal, and all metals at that. There is no doubt that the electrons are inside the metal. You can get them out in very many different ways.

Finally, in order to explain the galvano-magnetic effects, you have got to have something that carries so much electricity in proportion to its mass that it will be affected by a magnetic field.

DR. W. LASH MILLER: By asking a question, I do not want any one to think I am mixing up in this family quarrel. This is no place for a stranger. What I understood is that the theory made the ratio somewhere between 5 and 15×10^{10}, and nature made it 7×10^{10}, and all I want to know is, who made it first? Was this ratio known to those who made up the theory, or were they very much surprised to discover it?

PROF. RICHARDSON: I suppose that question calls for an answer. The ratio was known before the theory was invented. It was a slip on my part if I said predicted. I only meant to imply it was in agreement.

DR. D. F. COMSTOCK: It seems to me that those who have worked with physical theory realize the almost tremendous difficulties they have ahead of them. Difficulties are on every side, and it is necessary to expand the "function" into a series of terms, as in the case of Maclaurin's Theorem, and then determine one term at a time. In this way we reach a view which approximates closer and closer to the truth. This is what the physicists have to do.

Now I am always impressed when I come to any scientific meeting with the relatively large amount of well obtained data, and the relatively small amount of satisfactory explanation. Of course one does not expect a complete explanation or anything like it, but even "the first term of the series" is usually not forthcoming. In the experimental domain on the other hand, it seems to me that, although accurate data is sadly wanting in most directions, still the first term of the experimental series, as one might say, has been determined in most cases.

For my own part I feel in a constant state of awe at the complexity of nature, and sometimes it seems to me a very wonderful thing that we have any explanations at all. I am surprised that anyone ever made the first step. It seems to me more wonderful that a theory succeeds at all, than that it fails.

It may be that we have positive electrons in metals. It may be that we have a flow of ether in a wire. As far as I am con-

cerned, I am waiting for the proof of any view, but what I think is important here, as in all lines of human endeavor, is that we should get something *positive*. The work of the critic has its place. Of course brakes are necessary, and when the amount of theory-production comes to be half of the whole business, or even an appreciable fraction of it, then I believe in putting on the brakes, and putting them on hard, because this would not correspond to a wise division of labor, but at present sober theory-construction has gone on to a relatively small degree.

In a certain sense theories seem easy to put forward, and you hate to see a man get a prize or gain great reputation for something which does not require anything more physically than a pencil and the strength to push it, and perhaps you oppose him a little, unconsciously, for this reason. It is not true, however, that theories worthy of the name are easy to produce. The complexity of nature is such that a theory which covers more than one very small corner of observed facts is very difficult to produce, and should be very impressive.

Regarding the general division of 2 percent theory 98 percent experimental result, it seems to me that the discussion of two rival theories is a much more interesting thing than simply opposition to one theory. Criticise by all means, but the men who have worked on this thing and have given new views, which after all do cover "the first term of the series," Prof. Richardson and his associates for example, should be congratulated for what they have done. The truth of an idea is determined, as the Pragmatists say, by how well it works, and Prof. Richardson's view does work well part of the way at least, and this is very encouraging.

If anyone can produce them, let us have half a dozen theories. The only view which at present seems to have vitality enough to stand alone is the electron view which we have been discussing, and since in most solids and liquids the environment of the electrons must be extremely complex, there is ample possibility that the present theory may in the future be brought to cover the experimental anomalies discussed. You may say that the thing does not come out by the "electron theory," but the very words "electron theory" are vague. Although the general views are widespread, still there has been no definite agreement as to

just what we will call the "electron theory," and one man might get one result by it, and another man get another result, depending on the assumption each made regarding the electronic environment.

In my opinion we can advance in our knowledge on this subject only by free and open discussion of the various theories, and it seems to me the laws of the battle are such that a theory like the present one can only be annihilated by a combatant armed with another theory.

DR. WEINTRAUB: Of course, I admit the desirability of pursuing this investigation so long as the necessary respect for the facts is preserved and the results of speculation not given out as the final results of science. There is, however, one point in which I do not agree with Prof. Comstock. I do not believe that we have an overwhelming amount of well established experimental data. As a matter of fact everyone who has to look up data on any specific subject has the same experience. Either the data are absent or not reliable or carried out under circumstances which deprive them of importance. Just to mention a few things of importance, the conductivity of *pure* metals is not known, the exact effect of the changes in structure on the conductivity is not known, the data on the conductivity of oxides and other compounds at different temperatures are scarce and we do not know with surety the nature of their conduction. Who will deny that an exact knowledge of these things and of a host of others might not lead to new conceptions and who will deny that in absence of exact data, systematically obtained, our speculations are liable to be fruitless? We have but few data here and there but I believe we have plenty of "explanations."

PROF. R. A. MILLIKAN: We learn one thing at a time; we do not learn everything which is to be learned about a new theory the minute it is propounded. Now the electron theory explains some things very beautifully. There are other things which in the very imperfect state of our knowledge we do not yet see how it explains. This seems to me only a reason for looking into it more carefully rather than for discarding it. I am reminded by this discussion of an incident which recently occurred in my sister's family. The little seven-year-old boy came home one day

completely disgusted with the problem of acquiring knowledge. He said that for a week his teacher had been telling them that 5 and 2 made 7 and he had just got the darned thing learned when she told him that 3 and 4 make 7. (Laughter.)

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE INFLUENCE OF DIFFUSION ON ELECTROMOTIVE FORCE PRODUCED IN SOLUTIONS BY CENTRIFUGAL ACTION.

By W. Lash Miller.

In reading Tolman's account of his measurements of the electromotive force produced in solutions by centrifugal action,[1] I noticed that the equations for the electromotive force were deduced without allowing for any possible differences in concentration at the two ends of the tube produced by the whirling;[2] as in some of his experiments these differences would become very considerable if the rotation were sufficiently prolonged, it seemed possible that even in a few minutes the "concentration cell" effect might become measurable, and that it might perhaps account for the "residual electromotive force" observed by him.

The calculations carried out in the following paragraphs show, however, that the polarization produced by concentration changes in short periods of centrifuging is very slight. During the rotation both iodine and iodide keep increasing in concentration at the outer electrode and decreasing at the inner, but the E.M.F. that would be produced by an increase of one percent in the concentration of the iodine alone is almost counterbalanced by a rise of one-third percent in the concentration of the iodide; and, as will be shown, the iodine concentration rises, at first, just about three times as rapidly as that of the iodide; so that the E.M.F. actually generated is very small, much too small to account for the "residual" voltage observed by Tolman.

As, so far as I am aware, no attempts have hitherto been made to calculate the rate at which diffusion would take place under the influence of centrifugal force, a short account of the method which I have adopted may prove of interest. Briefly stated, it consists (*1*) in determining the distribution of concentrations along

[1] Proc. Am. Acad. Arts and Sci., 46, 109 (1910). Jour. Am. Chem. Soc.

[2] Acad., *loc. cit.* p. 116, foot note.

the tube when equilibrium has been reached (*i. e.*, when the solution has been whirled for an "infinite" time) by the usual thermodynamic method; (*2*) in treating this equilibrium as due to the equality of two "virtual" rates of flow, one (towards the axis) due to concentration gradient, and the other (toward the periphery) due to centrifugal force; (*3*) in expressing the former of these by Fick's equation for the rate of diffusion along a fall of concentration, and thus (*4*) finding a plausible expression for the second or virtual flow due to centrifugal force. Assuming, then, that the actual flow at any moment is represented by the algebraical sum of the two components, expressions for which have thus been obtained, (*5*) a differential equation is set up, and a solution obtained to suit the conditions of Tolman's experiments.

The method just described is employed in calculating the rate of diffusion of the potassium iodide in solutions originally normal with regard to the iodide and fiftieth normal with regard to free iodine, the effect of the small quantity of iodine on the diffusion of the iodide being neglected. In calculating the rate of diffusion of the iodine in the same solutions, however, it had to be remembered that, in the absence of centrifugal force and of iodine-concentration difference, iodine will diffuse from a dilute to a concentrated solution of potassium iodide. This fact, which is taken account of in the present system of chemical formulas by distinguishing between "dissolved I_2" and "$\overline{I_3}$," is here allowed for by introducing a third "virtual flow," that due to iodide-concentration difference, as explained below.

POTASSIUM IODIDE, CONCENTRATIONS AT EQUILIBRIUM.

The distribution of concentration along the centrifugal tube when equilibrium is reached is given by the expression

$$\mu - \frac{2\,\pi^2 N^2\,(1-vd)\,x^2}{981 \times 42660} = const. \qquad (1)$$

where μ is Gibbs' thermodynamic potential; it may be replaced by

$$\frac{1.98\theta}{F} log\ nat\ z + const.$$

[N is the number of revolutions of the axis per second; θ the thermodynamic temperature, 293 in Tolman's experiments; F the thermodynamic

formula weight, assuming 78 percent dissociation $F = 166/1.78$; z is the concentration of the iodide, as only ratios occur in the formulas, any units will do; v the "partial volume" (Tolman) of the iodide = 0.284; d, the density of the solution, = 1.115; $\pi = 3.1416$; the divisor 981 × 42660 converts ergs to calories; 1.98 is the gas constant.]

whence, neglecting the change of vd with the concentration,

$$[at\ equil.]\ z = Ae^{\beta x^2};\ where\ \beta = 5.180 \times 10^{-8} N^2 \quad (2)$$

Since the total amount of iodide in the tube remains constant,

$$\int_r^R z dx = z_0(R - r);\ whence\ A = z_0(R - r) / \int_r^R e^{\beta x^2} dx \quad (3)$$

[z_0 is the initial concentration of the iodide, uniform throughout the tube, (normal, in Tolman's work); r (Tolman's r_1) the distance of the inner electrode from the axis, and R (Tolman's r_2) that of the outer electrode, both in centimeters. As the outer electrode fitted the end of the tube and the inner electrode had almost the same cross section as the tube, r and R give the distance of the effective inner and outer ends of the column of solution from the axis. In the experiments with potassium iodide and iodine, $r = 4.3$ and $R = 29.40$]

The definite integral on the right may be evaluated by expanding $e^{\beta x^2}$ and integrating term by term. When $N = 82$ (the greatest speed in the potassium iodide experiments), $\beta = 3.484 \times 10^{-4}$ and $A = 0.898\ z_0$; hence when equilibrium is attained at a speed of 82 revolutions per second, the concentration of the iodide at the outer electrode will be 1.213 normal, and at the inner will be 0.904 normal, a ratio of 1.34 to 1.00.

POTASSIUM IODIDE, RATE OF DIFFUSION.

If the motor were stopped after the state of equilibrium had been attained, there would immediately ensue a flow of salt through the solution away from the peripheral end of the tube, the amount of which is given by

$$Concentration\ flow\ towards\ axis = k\frac{\partial z}{\partial x} \quad (4)$$

where k is the diffusion constant (cm^2, sec) of potassium iodide at 20° C. in normal or approximately normal solution. I have taken $k = 14.5 \times 10^{-6}$.

As explained above, this "concentration flow" may be regarded

as just balanced, at equilibrium, by the "centrifugal flow" in the opposite direction; the latter would therefore be represented by

$$\textit{Centrifugal flow toward axis} = -k\frac{\partial z}{\partial x}\textit{ at equil.,} = -2k\beta xz \qquad (5)$$

Thus an expression for the centrifugal flow at equilibrium is obtained, and it is assumed that (5) will hold whatever the distribution of concentrations; *i. e.*, that in general

$$\textit{Flow towards axis} = k\frac{\partial z}{\partial x} - 2k\beta xz \qquad (6)$$

When the motor is first started, $\frac{\partial z}{\partial x}$ will be zero, and the "flow" will be negative, *i. e.*, the salt will move towards the outer end of the tube; when equilibrium is attained the flow will be zero; and when the motor is stopped β will be zero, and the flow will become positive in sign, *i. e.*, the salt will move towards the axis.

The *accumulation* at any point of the tube, x cm. from the axis, will then be given by

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial x} - 2k\beta xz\right) \qquad (7)$$

which is the differential equation sought. It is subject to the conditions that, as no salt can enter or leave the tube, the "flow" at $x=r$ and $x=R$ must be zero, or

$$[\textit{at } x=r \textit{ and } x=R]\ k\frac{\partial z}{\partial x} - 2k\beta xz = 0 \qquad (8)$$

and, moreover, that at the beginning of the experiment the concentration has the uniform value z_0 throughout the tube, *i. e.*,

$$[\textit{at } t = 0]\ z = z_0 \textit{ for all values of } x \textit{ from } r \textit{ to } R \qquad (9)$$

A solution of (7) that will satisfy (8) and (9) will therefore give the concentration at any point of the tube at any moment after rotation has begun.

Such a solution can be arrived at by means of successive approximations; for the present purpose, however, the problem may be simplified by neglecting the very slight variations in the centrifugal flow caused by the slight changes in concentration

which occurred along the tube in Tolman's experiments. Equations (7) and (8) then become.

$$\frac{\partial z}{\partial t} = \frac{\partial}{\partial x}\left(k\frac{\partial z}{\partial x} - 2k\beta x z_0\right) \qquad (10)$$

$$[at\ x=r\ and\ x=R]\ k\frac{\partial z}{\partial x}qz - \beta x z_0 = 0 \qquad (11)$$

while equation (9) remains as before.

These three equations, viz., (9), (10) and (11), are satisfied by

$$\frac{z-z_0}{\beta z_0} = \frac{4l^2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2}\cdot\cos\frac{n\pi(x-r)}{l}\cdot e^{\frac{-n^2\pi^2 kt}{l^2}} +$$

$$\frac{8lr}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n-1)^2}\cdot\cos\frac{(2n-1)\pi(x-r)}{l}\cdot e^{\frac{-(2n-1)^2\pi^2 kt}{l^2}}$$

$$-(r^2 + rl + \frac{l^2}{3}) + x^2 \qquad (12)*$$

Replacing y by $\pi(x-r)/l$ in the cosine series

$$y^2 = \frac{\pi^2}{3} - 4\sum\frac{(-1)^{n+1}}{n^2}\cos ny$$

$$\text{and } y = \frac{\pi^2}{2} - \frac{4}{\pi}\sum\frac{1}{(2n-1)^2}\cos(2n-1)y$$

(given, for example, in Byerly's "Fourier's Series and Spherical Harmonics," pages 44 and 45), there results

$$x^2 = r^2 + rl + \frac{l^2}{3} - \frac{4l^2}{\pi^2}\sum\frac{(-1)^{n+1}}{n^2}\cos\frac{n\pi(x-r)}{l}$$

$$-\frac{8rl}{\pi^2}\sum\frac{1}{(2n-1)^2}\cdot\cos\frac{(2n-1)\pi(x-r)}{l}$$

whence, for small values of kt/l^2 such as occur in Tolman's experiments,

$$[for\ x=r]\ \frac{z}{z_0} - 1 = -\frac{4R+8r}{3\sqrt{\pi}}\beta\sqrt{kt} \qquad (13)$$

$$[for\ x=R]\ \frac{z}{z_0} - 1 = \frac{8R+4r}{3\sqrt{\pi}}\beta\sqrt{kt} \qquad (14)$$

*In (12) l is written as a contraction for $R - r$.

In a paper by T. R. Rosebrugh and W. Lash Miller (Jour. Phys. Chem. 14, 826 (1911) equation 21) it is shown that for small values of at

$$\sum_{n=1}^{\infty} \frac{1}{p} e^{-p^2 at} = \frac{\pi^2}{8} - \frac{1}{2}\sqrt{\pi at}, \text{ approximately}$$

where $p = 2n-1$. From this it may be deducted that when $p = 2n$, the series is approximately equal to $\frac{\pi^2}{24} - \frac{1}{6}\sqrt{\pi at}$.)

As β is proportional to N^2, it follows from (13) and (14) that the time needed to bring about any given small change in concentration at either end of the tube is inversely proportional to the fourth power of the rate of rotation. What is ordinarily considered a rapid centrifuge, running at 2,000 revolutions per minute, would take over half an hour to accomplish what Tolman's apparatus (82 rev. per sec.) did in one minute.

IODINE, CONCENTRATIONS AT EQUILIBRIUM.

In dilute solutions of iodine in normal potassium iodide (where, in the language of the theory of solutions, practically all the free iodine is present as $\overline{I_3}$ or KI_3)

$$[free\ iodine]\ \mu = const. + \frac{1.98\theta}{254}\ log\ nat\ \frac{w}{z}$$

where w is the concentration of the iodine (*i. e.*, of the total free iodine determinable by thiosulphate) and z that of the potassium iodide. Introducing this value of μ into equation (1), and neglecting the change of vd with the concentration, there results

$$[at\ equil.]\ \frac{w}{z} = Be^{\gamma x^2};\ where\ \gamma = 15.18 \times 10^{-8} N^2 \quad (15)$$

[For dilute solutions of iodine in potassium iodide solution Tolman finds $v = 0.2376$; $d = 1.115$ as before.]

Replacing z by its value from (2) gives

$$[at\ equil.]\ w = ABe^{(\beta + \gamma)x^2} \quad (16)$$

in which AB can be determined as A was in (3).

When $N = 82$, $\beta = 3.484 \times 10^{-4}$, $\gamma = 10.21 \times 10^{-4}$, $AB = 0.6345$; thus when equilibrium has been attained at a speed of

82 revolutions per second, the concentration of the free iodine at the outer electrode will be 0.0414 normal ($z_0 = 0.02$ normal), and that at the inner electrode 0.0130 normal, a ratio of 3.18 to 1.00.

IODINE, RATE OF DIFFUSION.

Regarding the flow of free iodine through the solution (towards the axis reckoned positive) as made up of three components, the first of these, that due to differences in iodine concentration, may be set

$$Iodine\text{-}concentration\ component = K\frac{\partial w}{\partial x} \qquad (17)$$

[Brunner's experiments (Zeit. phys. Chem. 58 22-28 (1907)) seem to show that K is about $\frac{2}{3}\ k = 9.7 \times 10^{-6}$; two direct measurements made here by Mr. Pirie, gave 10.4×10^{-6} and 11.6×10^{-6}. In the computations 10×10^{-6} is used.]

where K is the diffusion constant of free iodine in approximately normal potassium iodide. The second, due to centrifugal force, may be set (as in equation 5)

$$Centrifugal\ component = -2K\gamma xw \qquad (18)$$

the third is then determined, since at equilibrium the total flow is zero,

$$Iodide\text{-}concentration\ component = 2K\gamma xw - K\frac{\partial w}{\partial x}\ at\ equil.$$

$$= -K\frac{w}{z}\frac{\partial z}{\partial x} \qquad (19)$$

The differential equation for the free iodine is therefore

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial w}{\partial x} - 2K\gamma xw - K\frac{w}{z}\frac{\partial z}{\partial x}\right) \qquad (20)$$

the boundary and initial conditions being

$$(at\ x = r\ and\ x = R)\ \frac{\partial w}{\partial x} - 2\gamma xw - \frac{w}{z}\frac{\partial z}{\partial x} = 0 \qquad (21)$$

$$[at\ t = 0]\ w = w_0\ for\ all\ values\ of\ x\ from\ r\ to\ R \qquad (22)$$

A solution which fits the conditions of Tolman's experiments

may be obtained by writing z_0 for z in (20) and (21) and replacing $\frac{\partial z}{\partial x}$ by its value from (12), viz., $2\beta z_0 x$. Equation (20) then becomes

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial w}{\partial x} - 2K(\beta + \gamma)xw\right) \qquad (23)$$

which is the same in form as (7). Expressions for w at $x=r$ and at $x=R$ valid for small values of Kt/l^2 may therefore be obtained by substituting K for k, w for z, and $\beta+\gamma$ for β in (13) and (14).

ELECTROMOTIVE FORCE OF THE CONCENTRATION CELL.

The net result of passing a current of electricity through the tube, so that the outer electrode is cathode, is that for every 96,540 coulombs 127 grams free iodine are lost at the outer electrode and gained at the inner, and 0.486 × 166 grams* of potassium iodide are gained at the outer and lost at the inner electrode. Writing Z_R, Z_r for the concentrations of the potassium iodide at the outer and inner electrodes respectively, W_R and W_r for those of the free iodine, and assuming that the iodide is 78 percent dissociated, the E.M.F. at 20° C. due to the concentration difference will be

$$E.M.F. = 0.000099 \times 293 \times \log_{10}\frac{W_R Z_r}{W_r Z_R} - 0.000198 \times 293 \times 0.486 \times 1.78 \times \log_{10}\frac{Z_R}{Z_r} \text{ volts.} \qquad (24)$$

$$= 0.0126 \log \text{nat}\frac{W_R}{W_r} - 0.0344 \log \text{nat}\frac{Z_R}{Z_r} \text{ volts.} \qquad (25)$$

When the difference between Z_R and z_0 does not exceed one percent or so, $\log \text{nat } Z_R$ may be replaced by the right hand member of equation (14), and similarly with the other logarithms; this gives

$$E.M.F. = (R + r)(0.0284\overline{\beta + \gamma}\sqrt{Kt} - 0.0776\beta\sqrt{kt}) \qquad (26)$$

or, inserting the values of R, r, β, γ, K and k

$$E.M.F. = 1.034 \times 10^{-10} N^2 \sqrt{t} \text{ volts} \qquad (27)$$

*0.486 is the transport number of the cation in potassium iodide solution.

The following table gives the gain or loss at each electrode in percents of the initial concentration, and the resulting E.M.F. in millivolts, for Tolman's three experiments with potassium iodide and iodine; on the assumption that in each case the salt was evenly distributed throughout the solution before rotation began.

N	t Sec.	Iodine		Iodide		E. M. F. Millivolts
		Inner Percent	Outer Percent	Inner Percent	Outer Percent	
62	150	— 0.087	+ 0.144	— 0.025	+ 0.041	0.0049
76	210	— 0.154	+ 0.256	— 0.044	+ 0.074	0.0087
82	60	— 0.096	+ 0.159	— 0.028	+ 0.046	0.0054

After running for fifteen minutes at 82 rev. per sec. there would be a difference of one percent between the concentrations of the iodine at the two electrodes; but even then, owing to the simultaneous changes in concentration of the iodide, the E.M.F. would not reach 0.021 millivolt.

The University of Toronto,
February, 1912.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

POTENTIAL DIFFERENCES AT THE JUNCTION OF IMMISCIBLE PHASES.

By Reinhard Beutner.

Some four years ago Professor Haber and I[1] investigated the potential differences at the junction of two immiscible phases which are both electrolytic conductors. The usefulness of the results obtained and of the conceptions evolved in this work were confirmed in their application to bio-electric phenomena in a recent investigation carried out by Dr. Jacques Loeb and myself in the Rockefeller Institute for Medical Research.

I. Measurement and Calculation of the E. M. F's of Cells Formed of Solid Salts.

I will first discuss the measurement and calculation of the e. m. f. of cells formed of solid salts while no water is present. The effect of "phase potentials"—that is, potential differences between two electrolytic phases—is seen in this case in a most striking manner. The e. m. f. of cells such as:

$$\text{Ag} \text{ — solid } \text{AgCl} \text{ — solid } \text{AgBr} \text{ — } \text{Ag}$$

or

$$\text{Ag} \text{ — solid } \text{AgCl} \text{ — solid } \text{Ag}_2\text{SO}_4 \text{ — } \text{Ag} \qquad \text{(I)}$$

is strictly zero.[2] But if sodium salts are introduced into the latter cell, a considerable e. m. f. is produced. For instance, the cell:

$$\text{Ag} \text{ — solid } \text{AgCl} \text{ — solid } \text{NaCl} \text{ —}$$
$$\text{solid } \text{Na}_2\text{SO}_4 \text{ — solid } \text{Ag}_2\text{SO}_4 \text{ —Ag} \qquad \text{(II)}$$

gives an e. m. f. of about 0.53 volts. This e. m. f. is much higher than any that could be obtained from a combination of aqueous

[1] F. Haber and R. Beutner, Annalen der Physik **26**, 947 (1908).

[2] This had been found experimentally by R. Lorenz, before we started our investigation.

solutions without metals. The seat of this e. m. f. must be at least partially at the junctions of the salts, since the e. m. f. of (I) is zero, and only the introduction of the sodium salts gives rise to the e. m. f. of 0.53 volt.

I have measured the e. m. f. of (II) by different methods and have always found the same value. At about 300° C. the e. m. f. of such a cell can be easily measured, since solid salts, heated to this temperature, have a fairly good electrolytic conductivity. The resistance is rather high, but with the aid of a good electrometer the e. m. f. can be measured.

How are these potential differences at the junction of salts to be explained? Such conceptions as solution tension and ionic concentration, which are generally applied in the calculation of e. m. f's of combinations of aqueous solutions, cannot be used in this case, since the ionic concentration is not known for any solid salt. We should undoubtedly make use of the thermodynamic theory of the galvanic current, which is really the foundation of all physico-chemical theories in this field.

This simple principle, deduced by H. von Helmholtz in 1847, is as follows: The chemical or physical changes which a current sent through a system brings about in this system, are the cause of an e. m. f., since these changes require the consumption of a certain amount of energy. Work has to be performed, and this work is represented by a special counter e. m. f. which the current has to overcome. There exists an e. m. f. even if there is no current sent through the system from an outside source. If the poles or terminals of the system are short circuited, this e. m. f. will produce a current which causes such changes as will bring the whole system nearer to equilibrium.

The reason why the e. m. f. of system (I) is zero is that no changes of any kind are possible in it. The solid salts are immiscible and cannot react with each other. *All components of the system are in equilibrium with each other however they may be arranged.*

Let us now send an electric current through system (I) from the left to the right. Metallic silver from the left electrode will be changed into silver chloride, while from the silver sulphate metallic silver will be deposited on the right electrode. Hence at the two electrodes some fresh AgCl is formed and some

Ag_2SO_4 disappears. But the total change in the whole system is zero, on account of the electrochemical reaction taking place at the junction of AgCl and Ag_2SO_4, when Ag passes over from AgCl to Ag_2SO_4 so that some fresh Ag_2SO_4 is formed and some AgCl disappears. The junction of AgCl and Ag_2SO_4 is the seat of a potential difference which is equal and opposite to the two potential differences at the poles.

To render the matter clearer, I will write down the changes of the components of the system. Before we pass a current, the system may be represented as follows:

$$\begin{array}{cccccccc} Ag & Ag & Cl & Cl & \tfrac{1}{2}SO_4 & \tfrac{1}{2}SO_4 & Ag & Ag \\ & & Ag & Ag & Ag & Ag & & \end{array}$$

If we now pass a current from the left to the right, the new system produced is as follows:

$$\begin{array}{cccccccc} Ag & & Cl & Cl & \tfrac{1}{2}SO_4 & \tfrac{1}{2}SO_4 & Ag & Ag \; Ag \\ & & Ag & Ag & Ag & Ag & & \end{array}$$

The total change is therefore:

Metallic Ag → Ag in AgCl → Ag in Ag_2SO_4 → metallic Ag.

While there are three potential differences in this cell, their total sum is zero, since all the reactions compensate each other.

The reason why cell (II) gives an e. m. f. of about half a volt is that its components are not in a state of equilibrium in the same sense as those of cell (I). The solid salts of cell (II) may also be assumed to be immiscible, but equilibrium exists only on account of the order in which the salts are arranged. This arrangement is such that no two salts which are capable of reacting with each other are in direct contact. If, for instance, the solid Na_2SO_4 were removed from its place in system (II) and inserted at another place, there would be a reaction between NaCl and Ag_2SO_4, forming AgCl and Na_2SO_4.

Now, what happens if a current is sent through this cell from the left to the right? At the electrodes some new AgCl is formed and some Ag_2SO_4 disappears, just as in cell (I). But in cell (II) the reverse change from AgCl to Ag_2SO_4 (which in cell (I) occurs at the junction of the two salts) does not occur at

all, since the two silver salts are separated from each other by the two impermeable sodium salts. Hence the total sum of all the changes produced by the current in the system will not be zero in this case.

The original system may be represented as follows:

Ag	Ag	Cl	Cl	Cl	Cl	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	Ag	Ag
		Ag	Ag	Na	Na	Na		Na		Ag		Ag	

If we pass a current through this system from left to right, the new system produced is as follows:

Ag	Cl	Cl	Cl	Cl	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	Ag	Ag	Ag
	Ag	Ag	Ag	Na	Na	Na	Na	Ag			

Or if we pass a current through the original system from right to left, the new system produced is as follows:

Ag	Ag	Ag	Cl	Cl	Cl	Cl	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	$\frac{1}{2}SO_4$	Ag
			Ag	Na	Na	Na	Na	Ag	Ag	Ag	

Hence in the first case the changes produced by the electric current are the formation of fresh AgCl and fresh Na_2SO_4 and the disappearance of NaCl and of Ag_2SO_4, while in the second case exactly the opposite chemical change is produced by the passage of the electric current in the opposite direction, so that the cell is reversible. The equation of the reaction is, therefore:

$$Ag_2SO_4 + 2NaCl = 2AgCl + Na_2SO_4$$

and the direction of the electric current determines whether the chemical reaction occurs from left to right or from right to left in the above equation.

If there is no external source of electric current, and if the silver electrodes of the system are directly connected together by a wire so that the cell is shortcircuited, its e. m. f. must be such that the current produced by it causes formation of those two salts which are in equilibrium or will not react with each other. These are Ag Cl and Na_2 SO_4. This means that the silver electrode in contact with Ag_2 SO_4 must be the positive pole and this is really the case.

The e. m. f. can be calculated from the free energy of the

reaction. For most reactions between solid substances the free energy is practically equal to the heat of reaction. According to Thomsen the heat of this reaction is 24,690 calories or 103,350 watt-seconds or volt-coulombs, and since the reaction is brought about by the passage of 2 x 96,540 coulombs, the e. m. f. is 103,350 ÷ (2 x 96,540) = 0.535 volt.

According to Berthelot the heat of reaction is 23,200 calories, from which the e. m. f. is found to be 0.515 volt.

The e. m. f. was measured at two different temperatures, and the following results were obtained:

at 160° 0.532 volt.
at 310° 0.532 volt.

II. RELATION OF THE PHASE JUNCTION TO POTENTIAL DIFFERENCES.

Cells formed of saturated solution or molten salts behave in a very different way. For instance, let us make a cell in a manner analogous to cell (I), but containing saturated aqueous solutions, as follows:

$$Ag \text{ — sat. sol. } Ag\,Cl \text{ — sat. sol. } Ag_2\,SO_4 \text{ — } Ag.$$

This cell has by no means a zero e. m. f. As is well known it is a concentration cell with respect to the Ag ions. Nor can we assume in this case that all components are in equilibrium, as was the case with cell (II). The two miscible solutions will in fact diffuse into each other.

The same remarks hold good for a cell made up of molten electrolytes, like this type:

$$Ag \text{ — molten } Ag\,Cl \text{ — molten } Ag_2\,SO_4 \text{ — } Ag.$$

The two molten salts are miscible. There is no junction of phases here which could give rise to a potential difference which would compensate for the sum of the potential differences at the two electrodes. R. Lorenz investigated experimentally cells of this kind and found that they have a considerable e. m. f.

To generalize these results, we may state that:

Every junction of two immiscible phases is the seat of a potential difference. This potential difference is reversible and

thermodynamically defined if at least one ion is common to both phases.

For it will always be possible to make up a cell according to the scheme of cell (I). If the common ion is the cation M, a cell may be made up as follows:

metal — phase I containing M —
phase II containing M· — metal (III).

This system is in a perfect state of equilibrium. Its e. m. f. is zero like the e. m. f. of cell (I). Hence the "phase potential" at the junction of phase I and phase II must be equal and opposite to the difference of the potential differences at the poles.

We also conclude that:

The potential difference at the junction of the two phases does not depend in any way on ionic mobility, like the potential differences between miscible solutions, but they must have properties characteristic of potentials at metallic electrodes.

This similarity with metals is clearly shown by the fact that "phase potentials" may be used to produce an e. m. f. which corresponds to a chemical reaction. For this purpose the "phase potentials" or the phases must be arranged in a certain distinct way, as is done in cell II. The arrangement of cell II may be used to determine, by measuring its e. m. f., the free energy of reaction between solid $Ag_2\ SO_4$ and solid Na Cl.

Many other arrangements are possible for measuring the free energy of the same reaction. It is not possible to explain here how these different arrangements may be made up. The reaction between Ag_2SO_4 and Na Cl is only one example of the large number of reactions the free energy of which can be determined by the measurement of an e. m. f. In the case of many reactions I have carried out the experimental determination, while for many others I have developed the scheme of the arrangement of the experiment.

I wish to give here a few more examples of reactions between solid salts, the free energy of which was measured by means of similar cells.

Reaction: $Cd_2SO_4 + 2LiCl = CdCl_2 + Li_2SO_4$.

Heat developed: 18,240 cal., corresponding to 76,425 watt seconds.

E. M. F., calc.: 0.396 volt.
obs.: 0.406 volt at 235°.
0.419 volt at 125°.

Reaction: $BaCl_2 + 2KF = BaF_2 + 2KCl$.
E. M. F., calc.: 0.340 volt.
obs.: 0.310 volt at 305°.
0.315 volt at 302°.

Reaction: $SrCl_2 + PbF_2 = SrF_2 + PbCl_2$.
E. M. F., calc.: 0.315 volt.
obs.: 0.300 volt at 260°.
0.304 volt at 210°.

Reaction: $PbCl_2 + 2KF = PbF_2 + 2KCl$.
E. M. F., calc.: 0.210 volt.
obs.: 0.231 volt at 310°.
0.220 volt at 210°.

By means of these new galvanic cells reactions of the most different types may be measured; even *i. e.,* such reactions as the formation of a hydrate of a salt from anhydrous salt and water. I have however not been able so far to perform measurements of this last type, though I deem it very well possible. An independent control of a large number of thermochemical data would be possible if the E. M. F. of these new cells was measured, as I have shown in a theoretical paper not yet published.

III. NERNST'S LAW FOR PHASE POTENTIALS.

I now wish to call attention to another property of "phase potentials" in which they resemble potential differences at metals. Nernst has shown that the potential difference between a metal and a solution of one of its salts varies with the concentration of the solution according to a logarithmic law. Exactly the same rule holds good for "phase potentials" as was also predicted theoretically by Nernst.

Let c_1 be the ionic concentration in phase I of the ion common to both phases, and let c_2 be the ionic concentration in phase II of the same ion, then the "phase-potential" is equal to

$$\frac{R\,T}{n\,F} \ln \frac{c_1}{c_2} + \text{const}$$

where R is the constant of the gas law, T the absolute temperature, n the valency, and F the electric charge of a monovalent gram ion.

The proof of this statement is easy. The e. m. f. of cell (III) is zero. The potential difference between the left-hand electrode and phase I is, according to Nernst's theory:

$$\frac{R\,T}{n\,F}\ln c_1 + C_1$$

where C_1 is a constant, and the potential difference between the right-hand electrode and phase II is

$$\frac{R\,T}{n\,F}\ln c_2 + C_2$$

where C_2 is another constant. The difference of both volumes is the "phase potential" and therefore equals

$$\frac{R\,T}{n\,F}\ln\frac{c_1}{c_2} + (C_1 - C_2)$$

Haber first devised a method for directly demonstrating this property of "phase-potentials." The feature of the method is that one of the concentrations c_1 and c_2 is maintained constant, while the other is being varied. *This can be done, if the salt whose concentration is varied is soluble in one phase only.*

To fulfill this condition we use as phase I an aqueous solution of Hg NO_3 and as phase II an insoluble salt with the same ion, for instance, Hg Cl. We then measure the e. m. f. of the following combination:

Calomel electrode — solid HgCl — $HgNO_3$ aqueous solution — Calomel electrode.

If we vary the concentration of the $HgNO_3$ solution in this cell, the ionic concentration of the solid Hg Cl layer will not be affected. Nor will it have any considerable effect on the potential difference between the $HgNO_3$ solution and the right-hand calomel electrode, since no "phase potential" exists there. Hence the e. m. f. of the whole system must vary with the Hg concentration according to the logarithmic law, just as in the case of a metallic electrode.

This was shown by experiment to be very exactly true. The

concentration of Hg was changed over a large range by employing Na Cl solutions saturated with Hg Cl (instead of the $Hg\,NO_3$ solution). As is well-known the $\dot{Hg}$ concentration of such a Na Cl solution is exceedingly small and yet very accurately defined.

Experiments of the same kind were made with other insoluble salts, like Ag Cl and $Ca\,SO_4$, and their ions in aqueous solution, and the same results were obtained.

Further, Haber and Klemensiewics made experiments on phase potentials of this kind varying the $\dot{H}$ concentration. Both phases contained water in their experiments. For instance, if phase I is ice, and phase II is water, then only in phase II acids and bases are soluble, permitting a variation of the $\dot{H}$ concentration. For phase I, instead of ice, such materials as glass or solutions of water in organic solvents (like benzol) were taken. Haber developed a complete theory of the change of the potential difference, if the $\dot{H}$ concentration is also variable in phase I to a small extent.

IV. PHASE POTENTIALS IN LIVING TISSUES.

The phase potentials are of special importance for electric phenomena in animals and plants. Organic tissues are built up from cells surrounded by membranes. These membranes separate aqueous solutions of various substances (among them salts) from each other. Although the chemical composition is unknown, any membrane may be assumed to have a small[3] electrolytic conductivity. Then "phase potentials" will exist on both sides of the membrane.

Hence if we cut part of a tissue or take a whole organism and make connection at two points by means of non-polarizable electrodes to a measuring instrument, we will find in general an e. m. f. If we do not find any, we cannot conclude that there are no potential differences in the tissue, since it is more likely that potential differences exist, but that they are arranged in such a way as to compensate each other.

The fact is that in many cases a living tissue will give rise to an e. m. f. These bio-electric currents have been studied since

[3] Possibly of the order of a solid salt.

Galvani's famous experiment and the scientific literature relating to this subject is enormous. The aim of most of the research work done in this field was to establish relations between electromotive properties of tissues and vital phenomena, but very little has so far been known of the physical nature of these e. m. f's.

As to the order of magnitude of these bio-electrical forces, Du Bois-Reymond, who worked all his life in this field, has said that a complete physical explanation was impossible if attempted on the basis of an analogy with cells formed of aqueous solutions. Bio-electric forces resemble much more the e. m. f's. of cells with metallic electrodes. This seems strong evidence for the presence of "phase potentials" similar to metal potentials as explained before.

What is the nature of the "phase potentials" which make up the bio-electric forces? With respect to which ions are they reversible? In a recent investigation, Dr. Jacques Loeb and myself succeeded in solving this problem to some extent, and we did so by using the method which I described above. In the case of a layer of Hg Cl we know we have an electrode reversible with respect to Hg. With a membrane of unknown composition we cannot tell beforehand for which ion it will be reversible, but we can find it out, in the same way as we demonstrated the Hg reversibility of Hg Cl. The membrane is brought into contact with solutions of various salts and in various concentrations and the changes of potential are measured.

The difficulty was to find the right kind of a biological object. Dr. Loeb made the right suggestion by proposing to use parts of plants (fruits and leaves), because of their greater resistance to chemical agents. As a membrane especially, the outer skin of a fruit or leaf gave excellent constant results. The two ends of the leaf were placed in two solutions and from the solutions the current was led to the electrometer with the aid of calomel electrodes. Thus we tried solutions of K Cl, Na Cl, Ca Cl_2, Mg Cl_2, Ba Cl_2, Li Cl and others, and varied the concentration in each case *on one side*. The most remarkable fact established was that all salts showed the same effect upon the potential of the membrane; with decreasing concentration the solution the concentration of which was changed became more positive, and this occurred very nearly in the amount required by Nernst's

formula (the change of e. m. f. at room temperature being 0.058 volt when diluting ten times). The sign of the change shows that the potential is reversible for cations but it is not so for one single cation only, but all cations seem to act in the same way. A phenomenon like this has not yet been known in electrochemistry, but it may be very well explained on the principles given above. What the theory demands for a "phase potential" like this, in order to make it reversible for different cations, is the presence of the slightest amount of all ions in the membrane. For Na, K, Ca this may very well be the case. We can suppose the membrane to contain traces of Na, K, and Ca bound on fatty acids, proteins or carbohydrates in homogeneous mixture. The presence of Li and Ba, however, is not likely, but we can assume a chemical reaction to take place between the outer Li or Ba solution and the Na (or K or Ca) compound of the membrane causing an exchange. In this way we may also get a trace of the ions into the membranes.

The conclusion is to be drawn that salts are insoluble in all membranes for which Nernst's equation holds, as described. For if the salts are soluble in the membrane, an increase of concentration in the outer aqueous solution would also mean an increase of salt concentration in the membrane itself, the concentration ratio of salt in the water to that in the membrane would therefore not increase at all, or increase only slightly; it is this ratio that determines the potential difference according to the formula given above.

Now insolubility means impermeability of the membranes to the salts, as Nernst has shown very clearly. The impermeability of many membranes to salts has also been proved by other methods, such as osmotic experiments. It must, however, be said that Nernst's equation was not always found to hold true; for instance, not in the case of an animal's skin, hence the possibility of permeable membranes cannot be denied.

V. NERNST'S EXCITATION LAW AND THE POTENTIAL DIFFERENCES UNDER DISCUSSION.

It would seem as though the electrical properties of tissues hardly had much to do with vital processes. This view, however,

we may say, is likely to be wrong, although our knowledge of the nature of vital processes is still very incomplete.

As evidence for this statement, I would briefly refer to another electro-physiological phenomenon, namely the effect of alternating current upon movement (or generally speaking excitation) of tissues. It is known that a current changing its intensity can cause excitation, *e. g.*, the movement of a cut-out muscle of a frog. Nernst has shown that a quantitative relation between the intensity and frequency of all alternating currents which are just sufficient to cause the movement of the same muscle can be calculated if it is assumed that the maximum polarization on the junction of membranes is the real cause of the movement.

Now polarization of ordinary metallic electrodes by alternating current is first of all proportional to the intensity of the current, but the polarization also depends on the frequency. The reason is that with the same intensity of current the electric quantity (in coulombs or ampere seconds) which passes for each half period in one direction is, of course, the smaller the higher the frequency. Ordinary diffusion counteracts the changes of concentration. In order to bring about a certain change in the concentration against the forces of diffusion, a certain electric quantity must be passed in one direction, *i. e.*, the period must be above a certain length of time or the frequency must be below a certain limit. A detailed calculation shows that the maximum polarization is inversely proportional to the square root of the frequency. Hence, if we make experiments in which we vary both the intensity and frequency of the alternating current, we will find that the maximum polarization is always the same for all currents for which the quotient of the intensity and the square root of the frequency is constant.

Exactly this same rule holds good for different currents which are just capable of causing movement of the same frog's muscle. This physiological law can claim a considerable accuracy within certain limits. The question how polarization may cause movement is readily answered by analogy with the capillary electrometer. Polarization brings about a change of surface tension on the surface of mercury as well as on the single elements of

the muscle. That a change of surface tension may cause a movement in different ways is well known.

Polarization means change of concentration on junctions of phases. If a current passes through a muscle, these changes will take place by electrolytic processes, as is likely from Nernst's theory; but we cannot tell from this theory what is the nature of these changes of concentration. In the experiments with a leaf and an apple, as described, the concentration was artificially changed and the changes of potential thereby determined as to their nature and behavior.

This kind of polarization is by no means confined to plants. Electro-physiological observations by MacDonald[4] and others, which I cannot discuss here at length, prove very clearly that in the case of animal tissues a change of the concentration of *any* salt also changes the potential on the membranes. Nernst's theory of excitation proves that polarization is the cause of the movement of tissues. Hence we may conclude that with our experiments with leaves and apples we have roughly imitated one of the processes which takes place many thousand times in our nerves, and our muscles, when we move. This is, of course, only one small part of all those complicated physical and chemical processes which, as a whole, are called life.

In conclusion, it may be said that another proof has been obtained for the necessity of salts for vital processes. Dr. Jaques Loeb's experiments on physiological salt actions have furnished abundant material for further progress along these lines.

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New York City.

DISCUSSION.

Mr. Merle Randall: There is one thing I would like to point out in connection with this, and that is that these values of the electromotive force need not necessarily agree. If we take the von Helmholtz equation we will see that is so, and until the value of the free energy of these various compounds

[4] Mac Donald, Proc. Royal Society, **67**, 310.

has been determined independently, we cannot check the experiment and the observed values, with any degree of certainty. Whether the free energy is equal to the heat of reaction is a problem which is very much open at the present time.

DR. BEUTNER: This was the action only with solid salts, and I think the free energy is pretty nearly equal to the heat produced by the reaction, if such reactions whereof all participants are solid are concerned. There were no solutions, only solid salts, and according to the Nernst theory of heat, it is pretty nearly alike.

PRESIDENT WHITNEY: What is the significance of the zero temperature coefficient? You get the same voltage at two temperatures?

DR. BEUTNER: The zero temperature coefficient accounts for the same fact, that the energy or the heat quantities are equal according to the formula of von Helmholtz.

MR. WILLIAM C. BRAY: The values of the temperature coefficients should throw some light upon the question under discussion. If we examine the results given on the charts before us, we see in the case in which the calculated and observed electromotive forces show the best agreement, that the temperature coefficient is zero, as required by the Helmholtz relation. In the other three examples, the agreement between the observed and calculated e. m. f.'s is not so satisfactory, and in at least one case the temperature coefficient is not zero.

DR. BEUTNER: Dr. Bray's suggestion is perfectly correct, but according to my experience it is hard to carry out, since the values determined are not sufficiently accurate. The measurement of cells with such solid salts as fluorides and lead salts involves great experimental difficulties. Slight impurities of the salt or decomposition influence the e. m. f. very much. I have tried the application of the Helmholtz relation but without much success. The temperature coefficient is in most cases small.

A paper read at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

ELECTRICAL ENDOSMOSE.

By Wilder D. Bancroft.

Perrin[1] has made the generalization that all porous diaphragms become charged positively in a solution which is strongly acid and become charged negatively if the solution is sufficiently strongly alkaline. This is the same as saying that electrical endosmose will carry the acid solution through the diaphragm from cathode to anode and will carry the alkaline solution through the diaphragm from anode to cathode. I do not intend now to discuss whether this generalization is or is not absolutely accurate for all diaphragms; but I do wish to show how certain apparent exceptions may be accounted for.

If we take an acidified copper sulphate solution and a porous cup we find that electrical endosmose carries the solution through the walls of the cup from anode to cathode which is not the direction that Perrin's law would lead us to expect. On the other hand the solution passes to the anode if we substitute copper nitrate and nitric acid for the corresponding sulphates. The sign of the charge on a diaphragm depends on the relative adsorption of cation and anion, being positive if the cation is adsorbed to a greater extent than the anion and negative if the reverse is the case. Let us assume that for equal concentrations, hydrogen as ion is adsorbed somewhat more readily than sulphate as ion, while copper as ion and nitrate as ion are only adsorbed to a relatively slight extent. In that case the diaphragm will be charged positively in sulphuric acid and in nitric acid; but will be charged negatively in copper sulphate. Electrical endosmose will then carry sulphuric acid and nitric acid solutions to the anode and a copper sulphate solution to the cathode, which is what happens. An acidified copper nitrate solution will also move to the anode because hydrogen as ion will be the deciding

[1] Jour. Chim. Phys. 2, 601 (1904).

factor. The situation is different with an acidified copper sulphate solution, especially if the concentration of copper sulphate is high and that of sulphuric acid is low. Since the adsorption of sulphate as ion increases with increasing concentration, there will come a point at which sulphate as ion is adsorbed more strongly than hydrogen as ion. The charge on the diaphragm will then reverse and electrical endosmose will carry the solution through the diaphragm from the anode to the cathode, which is what happens experimentally. This enables us to explain some facts observed by Reed[2] ten years ago. A containing vessel was divided into three compartments by means of two porous diaphragms. In the anode compartment there was a copper sulphate solution (sp. g. 1.17) slightly acidulated with sulphuric acid. The other two compartments contained H_2SO_4 solution (sp. g. 1.17). "Immediately on closing the circuit and causing a current to flow through the apparatus both the volume and the weight of the solution in the middle compartment begin to rapidly increase and continue to increase at an apparently uniform rate as long as the current flows. Even with a current of about ½ ampere per square inch of cross-section of electrolyte, the increase in volume amounts to 1.7 c.c. in one hour." Electrical endosmose would carry the sulphuric acid solution from the cathode compartment to the middle compartment. At the anode compartment we should have the copper sulphate solution tending to be carried into the middle compartment while the sulphuric acid solution would tend to be carried back into the anode compartment. The total transfer through this diaphragm will therefore be the difference of the two and will depend on the actual conditions in the diaphragm at any moment. I am inclined to believe that there will be a flow of solution from the anode compartment to the middle compartment; but the details are not sufficiently accurate to enable one to be certain of this. It is clear, however, that there must be an increase in the amount of solution in the middle compartment and that electrical endosmose is the important factor in Reed's work.

Perrin[3] has found that a saturated solution of barium carbonate moved to the anode through a chromic chloride diaphragm.

[2] Trans. Am. Electrochem. Soc. 2, 238 (1902).

[3] Jour. Chim. Phys. 2, 643 (1904).

Since such a solution is slightly alkaline by hydrolysis, the movement is apparently in the wrong direction. This might be due to barium as ion being adsorbed to a greater extent than hydroxyl as ion. An experiment made for me by Mr. Briggs disproved this assumption, because a barium hydroxide solution moved to the cathode through a porous cup. The only possible explanation then was that this was analogous to the case of copper sulphate and sulphuric acid. Let us assume that hydroxyl as ion is adsorbed a little more readily than barium as ion while carbonate as ion is only slightly adsorbed. The total concentration in a saturated barium carbonate solution is low; but the amount of hydrolysis is not very large and so the ratio of barium to hydroxyl is rather large and we therefore have conditions favorable to barium being adsorbed more than hydroxyl. To test this Mr. Briggs took a barium chloride solution and added a small amount of barium hydroxide. This solution moved slowly to the cathode through a porous cup, which was not what it should have done; but we found that dilute acid behaved similarly with this diaphragm so that the alkaline solution does behave like a dilute acid. We hope to repeat this experiment some day using a chromic chloride diaphragm. It was also found that a barium hydroxide solution passes much less rapidly than a sodium hydroxide solution having the same hydroxyl concentration. Since we know that barium is adsorbed much more readily than sodium, this is exactly as it should be.

Müller and Bahntje[4] found that, in acidified copper sulphate solutions, starch and gum arabic did not move to the cathode and did not cut down the size of the copper crystals when the solution was slightly acid; but did both these things when the solution was made more acid. The movement of the colloid to the anode in a slightly acid solution is just what happened with the porous cup. Of course the reversal will come at different degrees of acidity with different colloids. In fact, Müller and Bahntje found that gelatine moved to the cathode in solutions in which starch moved to the anode. The effectiveness of gelatine in cutting down the size of lead crystals in the Betts process is due largely to the fact that the solution is markedly acid. It has been claimed that gelatine has no effect on the quality of

[4] Zeit. Elektrochemie, 12, 320 (1906).

the deposit from lead acetate solution; but this of course can only be due to faulty experimental considerations. To prove this Mr. Bennett, at my suggestion, made up two solutions containing 10 percent lead acetate and 5 percent acetic acid. To one solution there was added 1 percent of glue. The two solutions were then run in series, using lead electrodes, the current density being 0.3 amp/dm^2. The beneficial effect of glue was very marked.

Aluminum sulphate is often added to zinc baths to improve the quality of the zinc deposit. The explanation for this has been given by Schlötter.[5] "Since aluminum sulphate is dissociated hydrolytically, in aqueous solution, into sulphuric acid and colloidal aluminum hydroxide, the action of aluminum sulphate is clearly that of a colloid. We get a similar result when copper is deposited electrolytically in presence of aluminum sulphate." Though Schlötter does not mention it, it seems certain that the action of tin salts[6] in a copper bath comes under the same head. It seemed as though a good way of confirming this would be to predict in regard to an entirely new case. If we boil a ferric acetate solution we shall get a certain amount of colloidal ferric oxide. If we add this to an acidified lead acetate solution, it ought to cut down the size of the lead crystals obtained by electrolysis. Mr. Bennett was good enough to try this experiment for me. He made up the following solutions:

A. Ten percent lead acetate and 5 percent acetic acid.

B. Three g. ferric acetate and a few drops of acetic acid made up to 70 c.c. boiled and filtered.

In one breaker was placed 300 c.c. A and in a second 300 c.c. A + 50 c.c. B. The two solutions were run in series at 43° with a current density of 0.3 amp/sq. dm., using lead electrodes. The deposit was distinctly better from the solution containing colloidal ferric oxide, though the ferric oxide is not as efficient as gelatine.

Another point that we can now clear up is the electrolytic precipitation of black, pulverulent copper from a dilute copper sulphate solution. In my paper[7] on "The Chemistry of Electroplating" I was forced to leave this point unsettled. We know

[5] Galvanostegie, 1, 38, 51 (1910).
[6] Borchers: Elektrometallurgie, 3d Ed. 193 (1903).
[7] Bancroft: Jour. Phys. Chem. 9, 282 (1905).

that it is not due to the simultaneous precipitation of hydrogen because we get all the copper out of certain copper sulphate solutions as a good deposit when we are doing electrolytic analysis. It cannot be due to the low concentration because the concentration of copper as ion in a complex salt is much lower. If we have a dilute, nearly neutral copper sulphate solution, we shall have certain amounts of hydrolysis and a certain formation of colloidal cupric oxide. Within certain limits this will be beneficial to the deposit, just as a certain amount of gelatine is beneficial. If we get in too much gelatine, we get a black deposit instead of a brilliant one. If we get too much colloidal cupric oxide relatively to copper as ion, we shall also get a black deposit. The favorable conditions are a dilute and nearly neutral solution. When we are determining copper electrolytically from a sulphate solution, the excess of acid cuts down the hydrolysis to a negligible amount. Hydrolysis is also prevented if we have a complex salt of copper and if the solution is neutral or alkaline, there is normally no tendency for the colloid to pass to the cathode. The same reasoning applies also, to a greater or lesser extent, to other metals. Of course one is not justified in concluding that all black deposits are necessarily the result of hydrolysis.

Since the iso-electric concentration is the one at which the anions and cations are adsorbed in equivalent amounts, it follows that we cannot draw any conclusions in regard to single potentials from measurements of the iso-electric point except for the special and somewhat improbable case that we have a zero adsorption of anions and cations.[8] This is also the explanation for the flowing mercury electrode not giving true single potentials.[9] Another interesting consequence is that we can no longer maintain that the potential difference between a metal and an aqueous solution is a function of the concentration of the ions of the metal only. It will vary to some extent with the nature of the anion and with the nature of the other cations present in so far as these are adsorbed by the metal in question.

Cornell University.

[8] Cf. Billitzer: Zeit. Phys. Chim. **45**, 327 (1903); **48**, 513, 542 (1904); Drude's Ann. **11**, 902 (1903); Goodwin and Sosman: Trans. Am. Electrochem. Soc. **7**, 83 (1905).

[9] Smith and Moss: Phil. Mag. (6) **15**, 478 (1908).

DISCUSSION.

PRESIDENT WHITNEY: If you adopt this theory, you eliminate the characteristics which exist in the specific material in which endosmose is taking place. It seems to me we ought to know whether we are permitted to leave out of consideration the material itself, its own positive or negative character.

DR. W. D. BANCROFT: The specific nature of the substances comes in very markedly, owing to the differences in the degree of adsorption. We have made some experiments which are not entirely finished, showing the radically different behaviour of an alumina diaphragm and a silica diaphragm, so that the whole thing turns on the specific adsorption. This gives one plenty of margin, because the adsorption is specific to some extent.

A paper read at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

SMEE'S THEORY OF ELECTROLYTIC DEPOSITS.

By Wilder D. Bancroft.

In a copy of the second edition of Smee's Elements of Electrometallurgy, published in 1842, there are some observations on the relation between current density and size of crystals, which appear to have been entirely overlooked or forgotten. As the book is not readily accessible it has seemed worth while to quote a few paragraphs for the historical interest:

(147.) "The laws which regulate the deposit of every metal appear to be the same, and although very simple, yet they have cost me much labour for their development. The properties of which I have here to speak are strictly those which relate to the quality of the metal, which is so materially influenced by various circumstances. The reduced metal may be precipitated in three different ways; as a black powder, as a reguline metal (or, in other words, a metal having the properties of ductility and malleability), and lastly, as a crystalline deposit. Between these there are, indeed, other intermediate states, or mixtures of two different states, of which we shall hereafter take notice."

(148.) "Law I.—*The metals are invariably thrown down as a black powder when the current of electricity is so strong in relation to the strength of the solution, that hydrogen is evolved from the negative plate of the decomposition cell.*

"The different states which reduced metals assume, as well as the different varieties of each state, appear to be nothing but a difference of aggregation of the minute metallic particles of which they are composed; metals deposited in a black powder are, probably, in an infinite state of division; then, as a variety of this anaphous mass, we have a spongy material resembling, more or less, the colour of the metal, but the particles of which are still so fine, that it may be moulded with the fingers into

any shape we desire. As another variety of this deposit the spongy mass may be aggregated here and there into hardish lumps interspersed in the sponge, and this condition may be so far increased as to give rise to the form which is termed the sandy deposit. Such are the varieties of the pulverulent deposit, the first class of metallic reductions, comprising black powder, sponge and sand.

"The cause of these varieties appears perfectly obvious, for hydrogen and copper are deposited at the same time. In a former part of the work we had to treat at great length upon the power of adhesion, which this gas possesses, and if in this place we apply the same fact, we shall see that it will sufficiently account for every variety of the pulverulent deposit. If the hydrogen is evolved in very large quantities, we can easily imagine that it would envelope each ultimate particle of the reduced metal, and prevent the cohesion of the neighboring atoms. In conformation of this rationale, the metal in this state, notwithstanding its usual colour, is uniformly black, a fact perfectly in accordance with the properties of light. Any substance in infinite division must of necessity be black, from its not having breadth enough to reflect a ray of light, which requires certain definite dimensions, which philosophers have measured. If the hydrogen is evolved in smaller quantities, we can easily conceive that some of the atoms of the metal would be aggregated together, forming the spongy deposit; if on the contrary, the quantity of metal deposited far exceeds the quantity of hydrogen produced, we can easily see that more metallic particles would be in conjunction, and, therefore, the deposit would be much firmer. If, lastly, the hydrogen is almost nothing, we can also understand that the particles of sand would be still farther increased in size. Metals of all colours and properties exhibit the same phenomenon, even silver, platinum, etc., which are usually white, gold, which is yellow, and copper, which is red, together with other metals, obey this law, all being easily reduced as a black powder."

(149.) "Law II.—*Every metal is thrown down in a crystalline state, when there is no evolution of gas from the negative plate, or no tendency thereto.*"

"When I speak of no tendency to the evolution of the hydro-

gen, I mean, that the strength of the metallic solution is so great that either electricity of a much greater tension must pass, or the solution must be rendered of more easy decomposition, before gas would be evolved.

"This is in fact in strict accordance with the generally-known properties of bodies, for we find, universally, where bodies are deposited quite at their ease, and very slowly, that they have a tendency to assume each for itself some peculiar and definite form. In the deposition of a salt for instance, if it is suddenly precipitated, it always presents itself as a fine powder, which would appear to be almost in the ultimate state of division, but if the deposit takes place very slowly, it will assume some peculiar form. Nothing can be more complete than the analogy between the crystallization of a salt, and the crystallization of a metal, for both agree in their atoms requiring sufficient time to arrange themselves in their own peculiar way. The crystalline condition is not very generally adapted for the purpose of the arts, because the sides of each separate crystal do not firmly adhere to its neighbour, but it is most admirably suitable for coating a reguline deposit, adding a beauty and lustre which it is impossible to give in any other way. If, indeed, the crystals are very slowly formed, each one will have so slight an adhesion to its neighbour, that a piece held by its edge will break from its own weight, and we may even increase this property to such an extent that only solitary crystals may, here and there, be deposited. In the crystalline state, the brittleness of the metal would appear to be caused by the liquid wetting each separate crystal, and the interval caused by the film of water in the mass of copper, would account for the very slight adhesion that is found to exist."

(150.) "LAW III.—*Metals are reduced in the reguline state when the quantity of electricity in relation to the strength of the solution is insufficient to cause the production of hydrogen on the negative plate in the decomposition trough, and yet, the quantity of electricity very nearly suffices to induce that phenomenon.*"

"In fact, the reguline state is obtained in the greatest perfection when hydrogen is just at the point of evolution, but yet none is really given off from the negative metal."

(151.) "The reguline metal possessed of the properties of

flexibility, malleability, and elasticity, seems to be produced by such an arrangement of the ultimate particles of the deposited metal, that, being thrown down in exact apposition, they form a regular mass, presenting frequently at the back of the object, a similar uniform surface to that seen at the front. When we perceive in ordinary metallurgic operations that the same may vary very much in its properties, that at one time it may be flexible, at another elastic, and at a third brittle; and when we further perceive that the density of the same metal may vary, that a cubic inch at various times may even differ in weight, we must not be surprised that reguline metal formed by electro-metallurgical processes may vary in the same way, and, indeed, we do find that differences of the same nature really occur. To attempt the explanation of these things would lead us far beyond human knowledge, and carry us to the properties of the ultimate atoms of substances, for, doubtless, these differences are produced by variations in the arrangement of these particles; how otherwise can we account for the compression caused by hammering a solid body, or the increase of volume from annealing it? To obtain, however, the reguline metal in great perfection, we should carry on our process with such celerity in relation to the strength of the solution, that at every point of the negative surface, or that at which the metal is deposited, the action should be uniform, and atom by atom of the metal should be so quickly thrown down, that no time is allowed for the particles to follow their own fancies and arrange themselves in crystals. There are, indeed, many little circumstances which interfere with the apparent density of the reguline metal, thus the ultimate particles appear to be thrown down closer together at a low than at a high temperature."

(152.) "Dismissing theories, however, we must remember these facts; that the electric power in any solution, when barely sufficient for the production of hydrogen, causes the reduction of the metal in a malleable and ductile state; that the electric power, when not nearly sufficient to cause the appearance of the gas, throws down the metals in crystals; and, lastly, that the pulverulent is produced when there is evolution of gas."

From these and other paragraphs we see: That Smee saw the analogy between crystallization and electrolytic precipitation,

and that he knew that high current density and low concentration, p. 113, cause a decrease in the size of the crystals while a higher temperature gives rise to coarser crystals. He was wrong in believing that hydrogen causes the pulverulent deposit; but he is not the only man who has made that mistake. Not having the electrolytic dissociation theory as a guide, he could not of course see that a potassium silver cyanide solution was a limiting case of dilution of a silver salt; but it was over sixty years before anybody knew more about electrolytic deposits than Smee did.

Cornell University.

A paper read at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

A ROTATING CATHODE.

By C. W. Bennett.

In order to obtain samples of metals and alloys, by precipitation on a rotating cathode, with high current densities, for the purpose of studying their physical properties, a cathode has been designed and built, which will perform six thousand revolutions per minute, carry three hundred amperes, and operate continuously under these conditions. A sketch of the cathode, mounted with motor, rheostat, and accessories, is shown in Fig. 1. The whole apparatus was mounted on a frame of heavy boards, 2 x 8 in. (5 x 20 cm.), well braced and fastened, to prevent vibration. An inch and a half (3.75 cm.) steel rod was held by set screws in the two cast steel holders which were screwed securely to the vertical face of the support. Fitting over this steel rod were two collars, held in place by heavy set screws at the back. The extensions on these collars were notched to receive the two steel bars *H, H,* which were 24 x 4 x ½ in. (60 x 10 x 1.25 cm.). In front of these, and fastened to the collars were heavy steel plates, through which cap screws passed, clamping the bars *H, H,* at any desired position in the horizontal plane. In order to prevent vibration and change of adjustment, two heavy bars or stiffeners were bolted vertically between the ends of the bars *H, H.* By means of this arrangement, it may be seen that adjustment could be obtained around in the horizontal plane, and upward and downward in the vertical plane. The cathode *F* consisted of a length of aluminum pipe, one inch outside and three quarters inch inside diameter and nine or ten inches long (furnished by Mr. Blough of the Aluminum Company of America). A rubber stopper served to close the bottom. This tube was held in a one inch (2.5 cm.) hole in the brass connector *D,* by a set screw. The top end of the connector was tapped to receive a ⅝-in. (1.5 cm.) shaft. The cathode and connector are shown in

detail in Fig. 2. The shaft and cathode were mounted on the steel bars *H, H,* by two bearings, a simple babbitted one at the top, with a ball bearing *A,* and a roller bearing *B,* at the bottom. The shell of the roller bearing B, fitted into a water cooled collar *C,* which being bolted to *H* held the bearing in place. At high speed of rotation it was found necessary to cool this bearing, hence the hollow collar was cast.

A detail of the bearings, water cooled collar, and an assembly of these are shown in Figs. 3 and 4. In using generator circuits

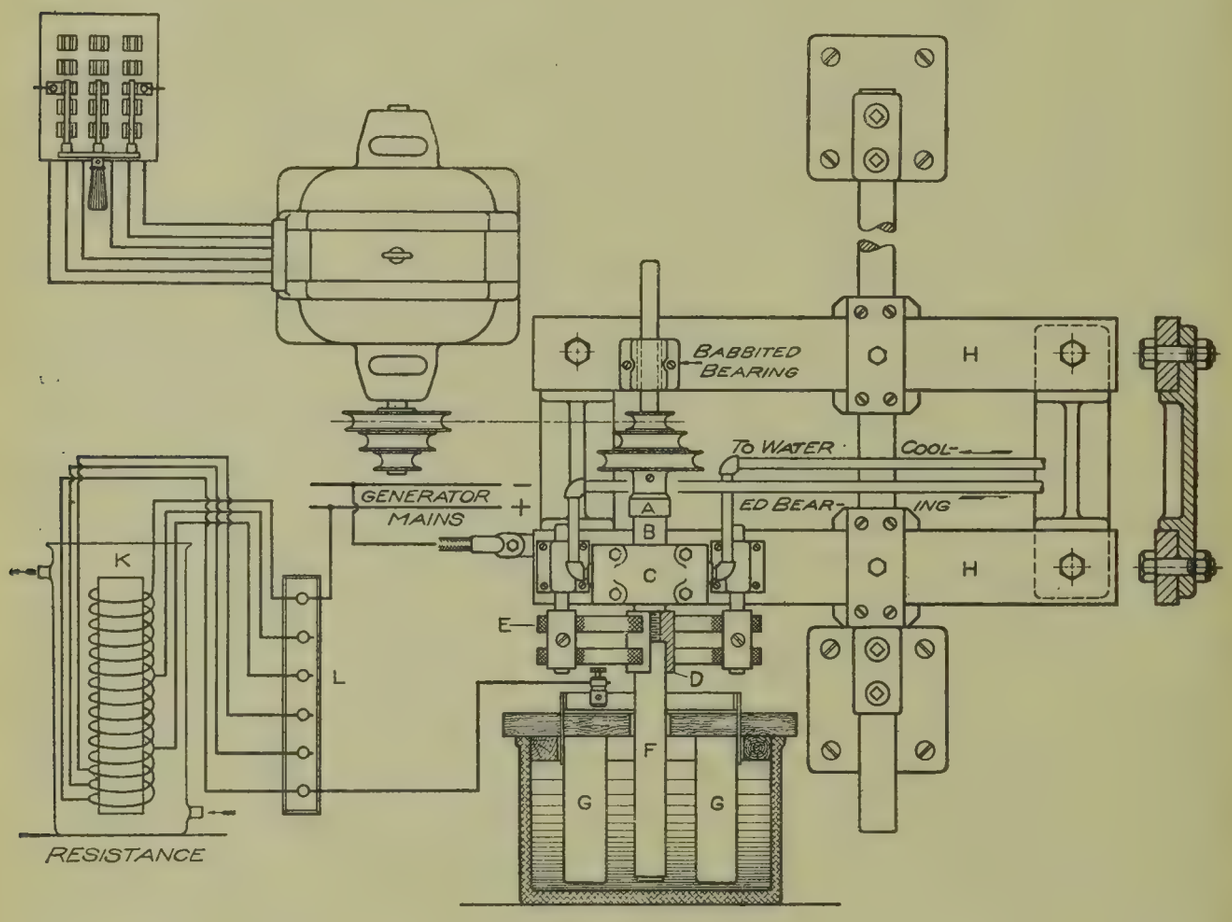

FIG. 1.

where the positive side is grounded for lightning protection, it is necessary to insulate the pipe delivering water to this collar. This was accomplished by inserting in the line a short length of garden hose. The discharge pipe was prevented from touching the sewer pipe by slipping a rubber tube over the end for a short distance. Above the ball bearing *A,* Fig. 1, a collar was fastened to the shaft. This held the shaft up in the bearings. This collar ended at the top in a horizontal plate which was screwed to the cone pulley, serving to hold the latter in place.

The electrical connection was made by means of a copper bar 0.3 sq. in. (1.9 sq. cm.) cross section, bolted to *H*, just behind the collar *C*. The contact surface was slightly over three square inches (19 sq. cm.). On opposite sides of *D*, and receiving the current from the cathode, were brushes *E*, consisting of thin plates of copper laid one upon the other, aggregating sufficient

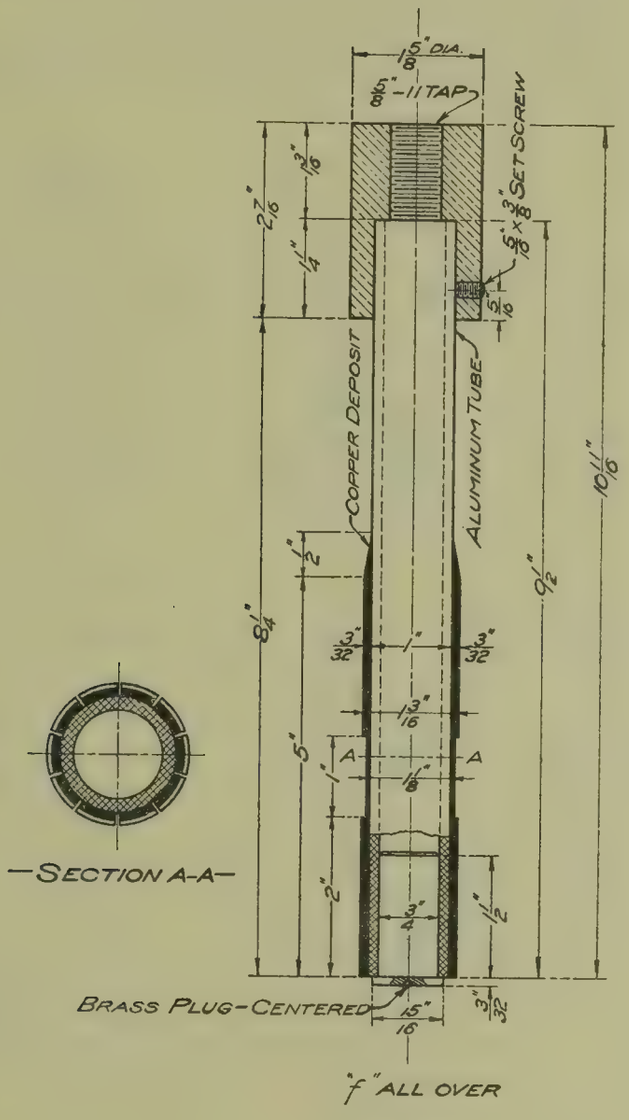

FIG. 2.

size to carry 300 amperes. These were mounted, as seen, in holders which were in turn bolted to the front of *H*.

The anodes, *G*, *G*, consisted of two bars of metal about 7 in. (17.5 cm.) long, 2½ in. (6.3 cm.) wide, and 1 in. (2.5 cm.) thick. To these were bolted strips of copper which extended through a narrow slit in the cover of the container for the electrolyte. These strips were connected by another strip to which the electrical connection was made. The cathode *F* rotated in a

1¼ in. (3.1 cm.) hole in the center of the cover. The cover consisted of a circular board 1 in. (2.5 cm.) thick, with a circular strip screwed to it, which fitted snugly inside the two gallon earthen-ware jar which was used for a container. This arrangement gave practically a seal for the jar so that there was no loss of electrolyte. Then too the anodes acted as baffle plates to break the excessive rotation of the liquid, the most rapid rotations being made without splashing the solution out.

The motor for rotating the electrode was mounted on the same

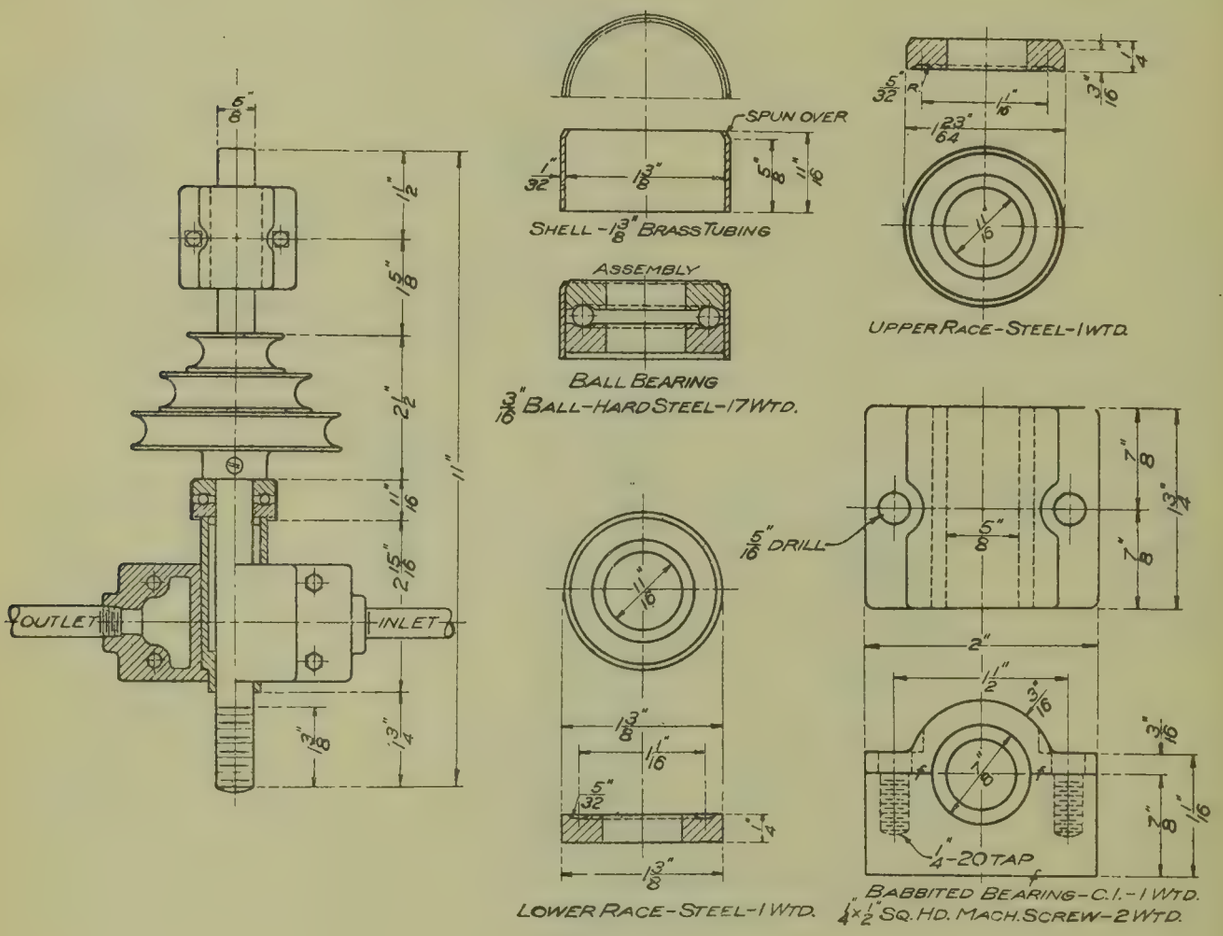
OUTLET
INLET
SPUN OVER
SHELL - 1⅜" BRASS TUBING
ASSEMBLY
BALL BEARING
⅜" BALL - HARD STEEL - 17 WTD.
UPPER RACE - STEEL - 1 WTD.
⅝" DRILL
LOWER RACE - STEEL - 1 WTD.
¼-20 TAP
BABBITED BEARING - C.I. - 1 WTD.
¼"×½" SQ. HD. MACH. SCREW - 2 WTD.

FIG. 3.

frame with the apparatus previously described. It was found to require about one-half horse power to rotate the cathode 6,000 R. P. M. when immersed to a depth of about five inches (12.5 cm.) in the electrolyte.

Where a rheostat was necessary, the arrangement *K*, Fig. 1, was found to be handy, flexible, cheap, and very compact. A post of wood held a spiral of No. 15 nickel wire by means of small screw eyes spaced equally around it. The wire was thus held out from the wood so that water could run in at the bottom,

circulate around the wire and discharge at the top. From various points along the nickel spiral, copper leads were brought out to the binding posts at *L*. By changing these connections which could be done by a sliding switch the current could be raised to a desired point gradually. This device carried 150 amperes and dissipated about 10 kilowatts of energy as heat, without the slightest inconvenience. The wire would no doubt carry 300 amperes. However for currents of 300 amperes a separately excited machine operating at any desired voltage,

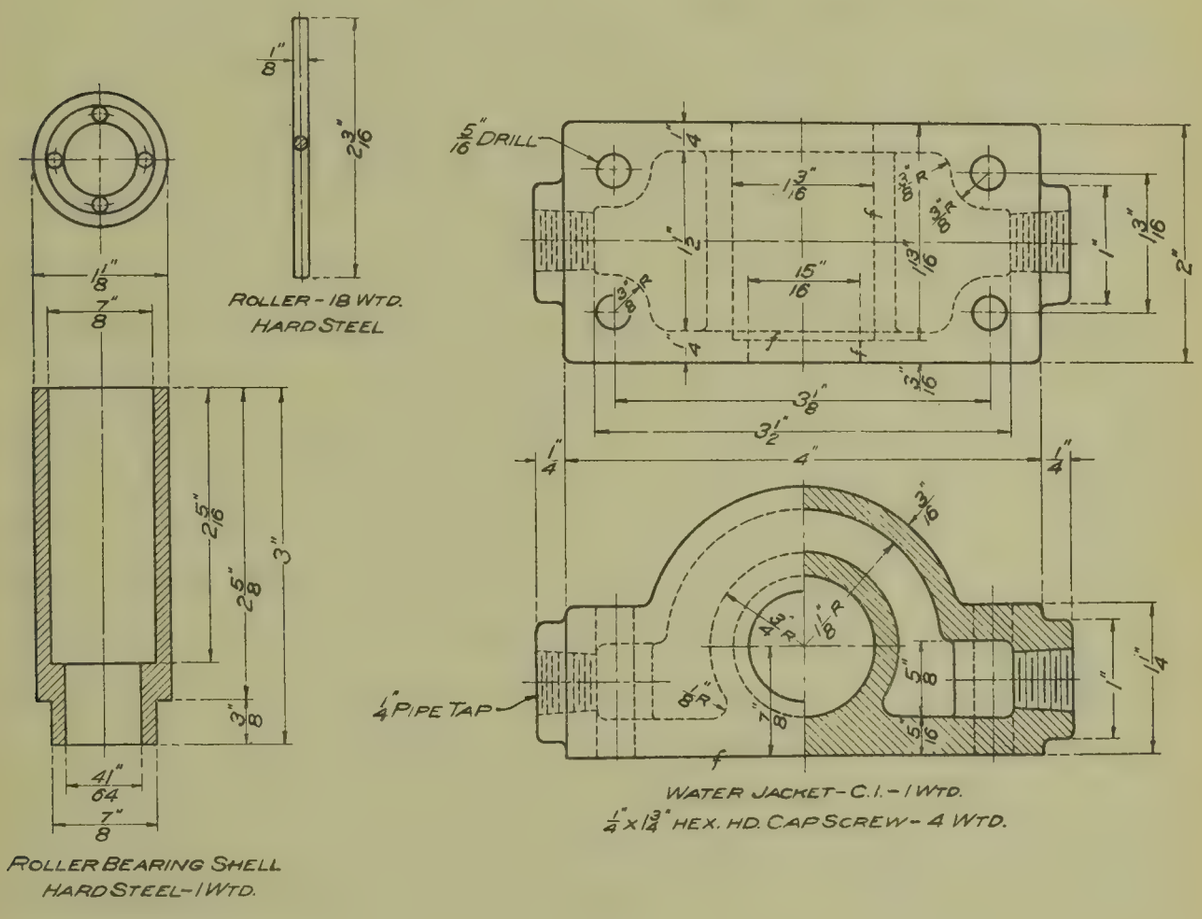
ROLLER - 18 WTD.
HARD STEEL
ROLLER BEARING SHELL
HARD STEEL - 1 WTD.
WATER JACKET - C.I. - 1 WTD.
1/4 x 1 3/4" HEX. HD. CAP SCREW - 4 WTD.
1/4" PIPE TAP

FIG. 4.

was used and hence the resistance was cut out. The total volume of this rheostat, to carry 300 amperes, need be only about ¼ of a cubic foot (7.5 cub. dm.).

The aluminum as shown in Fig. 2 was found to be an ideal metal upon which to deposit other metals, it being covered with a voluntarily acquired film of oxide, which obviates the necessity of treating the cathode to prevent sticking of the deposit. The metal, of course, is deposited in a cylindrical shape of any desired thickness about the pipe of aluminum. In order to get

this cylinder of metal off whole a thin shell of Rose's metal was cast around the aluminum. When the deposition was complete, the whole was dipped in boiling water, the alloy melted, and the metal cylinder lifted off. However, for physical tests, it being unlikely that the whole tube would be desired, the metal was deposited directly on the aluminum, and the following method adopted for getting strips of the metal for tensile strength and ductility tests.

As can be seen from Fig. 2, the connector holding the aluminum pipe was unscrewed from the shaft, the rubber stopper was removed from the lower end of the pipe, and a brass plug which was "centered" and tapered from the "centered" end, was driven in. The taper was so arranged that by slight pressure the plug fitted tightly inside the aluminum pipe. This done, the connector was "chucked" in a metal lathe, the center pin run up on the centered plug, and a section about an inch wide turned down in the center *A, A,* Fig. 2, to constant thickness. The whole was then removed and placed, in the same way as before, in a milling machine. Cuts were then made lengthwise through the metal as shown in Fig. 2 section *AA*. These strips were then pried off with a screw driver, the edges dressed down with a file, when, after measurements of the cross section, they were ready for physical tests. It was found more economical both of time and aluminum pipe, to cut almost through the copper to the aluminum below, on all save the last cut, where the fine adjustment of the machine was used and the copper cut completely through. After removing the metal the strips were broken apart by bending back and forth upon themselves. If a deep cut be made in the aluminum pipe, it is necessary, in order to get a perfect cylinder deposited the next time, to replace the pipe by a new one.

In conclusion, it may be said that:

1. A revolving cathode has been built which,

(*a*) Will operate at speeds up to 6,000 R. P. M.

(*b*) Will carry 300 amperes, giving a current density of about 3,500 amperes per square foot when 4 inches of the cathode is receiving a deposit. (385 A. per sq. dm. on 10 cm.)

2. The metal can be removed in nice shape for testing physical properties, without subjecting to strain of bending or heating.

This cathode was built at the suggestion of Professor Bancroft.

Electrochemical Laboratory,
Cornell University.

A paper read at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

TENSILE STRENGTH OF ELECTROLYTIC COPPER ON A ROTATING CATHODE.

By C. W. Bennett.

As early as 1865,[1] it was noticed that during electrolysis, if the cathode were rotated, a higher current density could be used. Among those actually making use of this was Wilde, who patented a process in 1875, using for cathode a vertical iron cylinder which was rotated. The current density used in this process was never more than 20 amperes per square foot (2.2 A. per sq. dm.).

The next important commercial application of this principle was the Elmore process. In this, the cathode was a mandrel, rotating vertically, over which agate burnishers rotated, keeping the deposited copper tubes smooth, and of constant thickness throughout. This process is used commercially in Europe at present in the manufacture of seamless copper tubes. The current density used is not more than 30 amperes per square foot (3.3 A. per sq. dm.). The copper thus obtained has a tensile strength of from 36,000 to 50,000 pounds per square inch (25 to 35 kg. per sq. mm.) depending, it is stated, on the speed of rotation.[2] However a part of this increase in tensile strength, over that of copper precipitated on a stationary cathode, is most likely due to the increase in the rate of burnishing, for we have here a true analogue to the process of rolling. Due to the increased rate of rotation, the tube passes under the agate burnisher faster, thus giving more and more, an approximation to the cold rolled copper, with its correspondingly higher tensile strength. The Dumoulin process substituted a burnisher of sheepskin for the agate of the Elmore process. It was claimed

[1] See Electrochemical and Metallurgical Industry, 6, 412 (1908), for review of these processes.

[2] Electrochemical and Metallurgical Industry, 3, 83 (1905).

that the animal fat insulated the projections, thus tending to give a more even surface. The current density was run up to 40 amperes per square foot (4.4 A. per sq. dm.). No mention is made of the strength of the deposit. This was tried commercially in England but failed completely.

Emerson in 1899 patented a process[3] for making a copper wire by plating copper on a rotating mandrel, wound around with a spiral of insulating material. The strip between the insulating material was then pulled off and drawn down. In 1899 he likewise patented a process[4] for making copper bars. A copper strip was wound spirally around a cathode which was rotated. The strip was thickened to a bar by depositing the copper on it while rotating. A large [*sic*] cathode was rotated slowly.

S. O. Cowper-Cowles patented[5] practically the same process, using a smaller cathode and rotating it more rapidly. The United States patent called for a process using a cathode moving "at such a rate of speed that will cause the hydrogen bubbles to be thown off from the metal deposited on the cathode, and cause such friction between the metal deposited on the cathode and the electrolyte as to yield tough and smooth deposits."[6]

Using a cathode twelve inches (30 cm.) in diameter rotating 1,000 R. P. M., and an electrolyte of 12.5 percent copper sulphate and 13 percent sulphuric acid, at about 70°C., with a current density of 200 (preferably 170) amperes per square foot (22 to 18 A. per sq. dm.), copper foil was obtained which was even stronger than the best cold worked copper. The results would have been more conclusive if a thicker deposit had been precipitated and tested. The liability to error will be apparent when the thickness of an average sample is considered. This is given,

Dimensions	Area	Tensile Strength
1.109 x 0.006 in.	0.0066 sq. in.	51,000 pounds per sq. in.
27.7 x 0.15 mm.	4.12 sq. mm.	35.7 kg. per sq. mm.

These results, as given, mean absolutely nothing in themselves, as will be seen below in the work on brass and bronze.

[3] U. S. Patent, No. 395,773, January 8, 1899.
[4] U. S. Patent, No. 638,917, 1899.
[5] English Patent, No. 26,724, 1898. U. S. Patent, No. 644,029, February 20, 1900.
[6] Mineral Industry, 9, 229 (1900).

Five reasons are given for rotating the cathode:

1. The electrolyte is stirred and impoverishment is prevented.
2. The copper is burnished by the friction with the electrolyte.
3. Foreign matter is eliminated, thus preventing "tree formation."
4. Air bubbles are brushed away, thus preventing "nodule formation."
5. Thickness of deposit is uniform.

There is little doubt that all of these factors enter into and tend to increase the tensile strength, and to enhance the character of the deposit. However, it seems highly improbable that the factors given above are the only ones entering into the equation. For this reason, it was deemed expedient to make some experiments, to see if other factors could be found, and to find their true relation to the tensile strength of the deposit. Then the principle was to be applied to the brasses and bronzes, with the hope that alloys of high tensile strength would be obtained.

With the copper the various factors were studied by holding others constant and varying one for a series of runs. In this way the effects of speed of rotation, current density, concentration of electrolyte, and temperature were determined. The apparatus consisted of an electrode holder designed to rotate continuously at any speed up to 6,000 R. P. M., and carry 300 amperes. This has been described in another paper.[7]

For currents up to 150 amperes, the 110 volt circuit, from the University power house, was used. For the higher current, a motor generator set was used.

The test pieces were prepared by the general method outlined in the previous paper referred to above. These pieces ran from 0.040 to 0.060 inch (1 to 1.5 mm.) thick. The actual deposit before turning down was much thicker. The measurements of the cross section were taken with micrometer calipers, reading directly to 0.001 inch (0.025 mm.). These pieces were then broken in an Olsen testing machine. Five or more tests were made, and their average taken as the true tensile strength.

During the runs it was found necessary to burnish the deposit once or twice. A mechanical burnisher was not desirable, for

[7] This volume, p. 245.

it would be open to the objection that the copper was being "rolled" as in the Elmore process. Therefore it was deemed best to stop the run once or twice, depending on the relative rate of stirring and on the current density, and burnish with emery paper. This was done by holding the paper against the rotating tube. The surface was then washed, treated with a strong solution of potassium cyanide to remove grease, and then with 1:1 nitric acid solution to slightly roughen the surface and insure the adherence of the next layer of copper deposited.

In general, if a solution be stirred during crystallization, the crystals resulting are smaller than those from the same solution without stirring, because more nuclei are formed. In depositing a metal, then, if it be precipitated directly in the crystalline state, we shall expect to get smaller crystals if the solution be stirred vigorously. However, the precipitation of the metal in the crystalline state directly is not at all probable. It is likely that the metal comes down in a condition analogous to a "melt," and then crystallizes from this. By rotating the cathode the uncrystallized material is agitated and smaller crystals result. The force of the rotation tends to move the material, forcing it to develop new crystal centers, and in this way prevents the growth of large crystals. Hence in precipitating copper, smaller crystals were expected from the run where the rotation was rapid.

It is also known that the tensile strength of steel, copper, etc., is increased by rolling. Rolling, it is generally admitted, does nothing more than break down crystal aggregates, giving a more finely crystalline mass. Hence, with the precipitated copper an increase of tensile strength was expected with a decrease of crystal size, as the rotation was increased. When this was tried the results showed that the theory was correct.

A solution containing 20 percent $CuSO_4.5H_2O$, and 12 percent H_2SO_4 was used. The temperature at starting was 35°C. This was desirable, for trial showed that this was the temperature maintained throughout a run at the current density used, *i. e.* 500 amperes per square foot (55 A. per sq. dm.). The deposits were treated alike, and every precaution was used to keep all conditions, save speed of rotation, constant. Results for four runs are tabulated below:

Current Density 500 Amperes Per Square Foot.

Revolutions per Minute	Voltage	Tensile Strength in Vertical Direction		Tensile Strength in Direction of Rotation	
		Pounds per Sq. In.	Kilo per Sq. Mm.	Pounds per Sq. In.	Kilo. per Sq. Mm.
1,750	3.2	37,000	25.9	.....	....
2,500	3.8	49,000	34.3	41,000	28.7
3,500	4.7	51,000	35.7	51,000	35.7
5,500	..	58,000	40.6	66,000	46.2

See Fig. 1 for curves representing these results. The voltage curve in Fig. 1 will be discussed later.

A gradual increase in the tensile strength, with increased rotation of the cathode, is seen from the curves. There has been

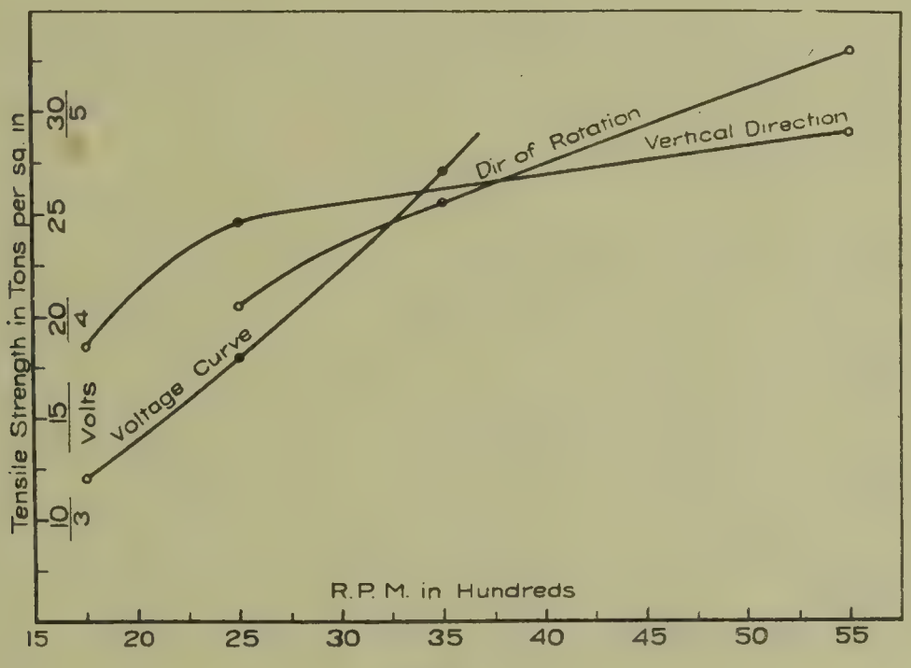

FIG. 1.

therefore a gradual decrease in the size of the crystals due to the increased rate of agitation of the uncrystallized matrix.

The observations given in the last column, were taken to show that the theory, assigning the increase in tensile strength to the mechanical deformation of the crystals or particles of copper, by the friction against the solution, is untenable. This theory states that the particles are drawn out in the direction of rotation, and a fibrous interlacing mass is obtained. According to this, the tensile strength would be greatest in the direction of the lamination. The test pieces in the form of rings, were cut off the bottom of the tube, while it was in the lathe. These were

broken by applying pressure in the direction of a tangent. Fig. 2 gives a sketch with detail of the apparatus used for these tests.

This was prepared in the following way. A disk of steel 1 in. (2.5 cm.) diameter and 9/16 in. (1.7 cm.) thick was sawed through with a hack saw, in the middle, giving two half disks. Holes were drilled in these, as shown in the figure, a little to the right and left of the centers of gravity of the sections. These were then fastened in two forks or brackets by pins, as shown. The brackets could then be held in the testing machine,

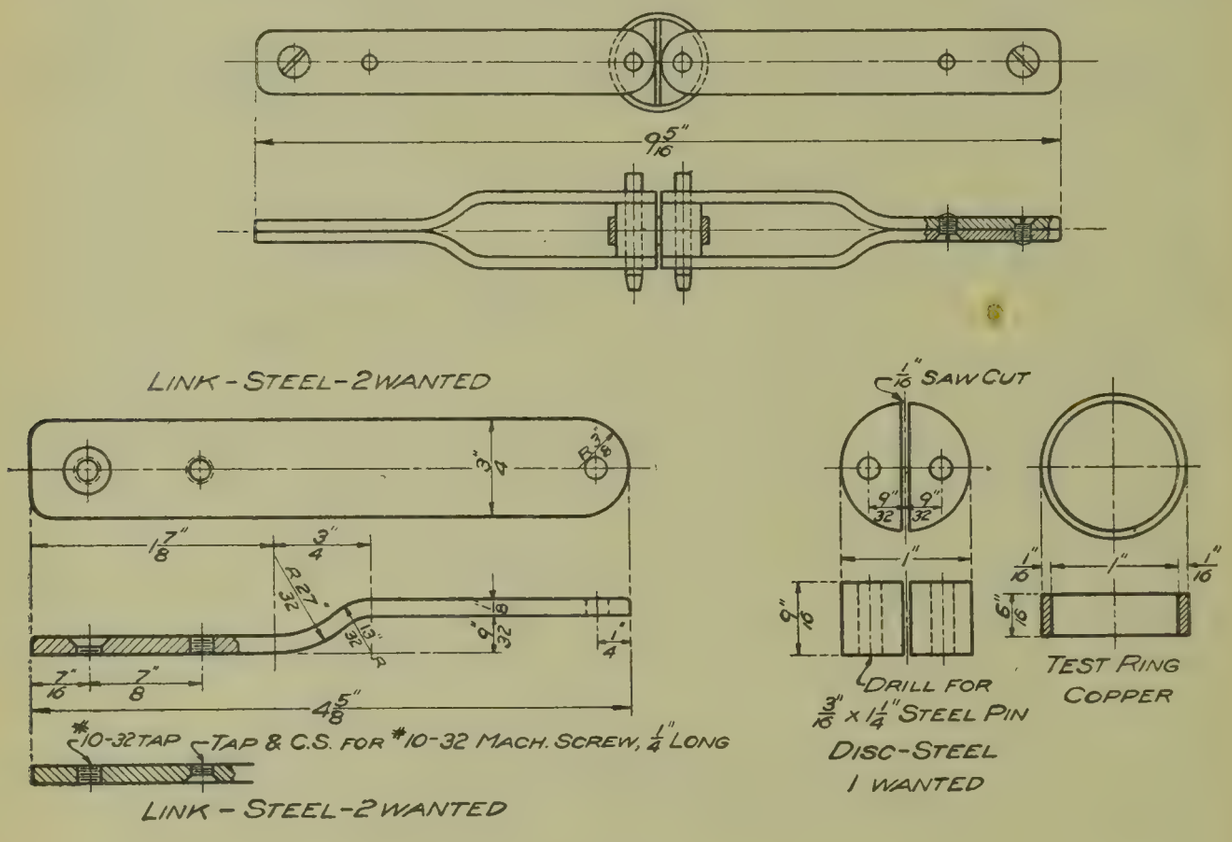
LINK - STEEL - 2 WANTED
LINK - STEEL - 2 WANTED
#10-32 TAP
TAP & C.S. FOR #10-32 MACH. SCREW, 1/4" LONG
1/16" SAW CUT
DRILL FOR 3/16" x 1/4" STEEL PIN
DISC - STEEL 1 WANTED
TEST RING COPPER

FIG. 2.

the ring of copper slipped over the disc sections, the brackets pulled apart and the ring broken.

The breaking load was then divided by two, thus assuming that it was evenly divided. In the last run, at 5,500 R. P. M., the difference is a bit greater than the experimental error and needs a little comment. At this rapid rate of rotation the solution is very violently agitated, and very fine bubbles of air are carried down into the solution. These are to some extent, most likely, entrapped and occluded in the copper. Now the bottom end of the cathode would receive the least amount of this air, and here the most compact deposit would be found, and con-

sequently the tensile strength would be highest. This is the most probable explanation, for, on examination, the texture of the deposit at the end proved to be finer. Anyway, if the theory were true, all the measurements should be higher than those on the vertical strip, by an amount depending on the speed of rotation. Since they do not show this general tendency it may be concluded the deformation of the crystals is not a factor.

In order to check up the inverse ratio of crystals size and tensile strength this series was polished, etched with ammonium hydroxide (1:3), and the crystal sizes and shapes noted under microscope. It was hoped that the measurements of the actual size of the crystals could be obtained, but they were so small that the results would have meant nothing had they been taken. However, in passing along the series rapidly a decrease in the crystal size could be detected. When they were mixed, one could arrange the series by noting the crystal size under the microscope. No difference in the shape of the crystals could be seen, as would be expected according to the deformation theory. Again the structure of the piece, from planes at right angles to each other, appeared to be the same. With the higher rates of rotation the deposit was smoother and better, showing that there was more efficient stirring and hence less impoverishment.

In Fig. 1, a curve is given, showing the voltage drop across the cell at varying speeds of rotation. An astonishingly large increase in voltage with increase in rotation is noted. The increase was more than was anticipated. It may be due to an increased resistance of the cell, or a back electromotive force. Increased resistance of the cell may be caused by an increase in the resistance of the brush contact, an air film on the cathode, or a tendency for the electrolyte to concentrate in the outer portion of the cell by being subjected to centrifugal force. These tendencies would increase with increased rotation. The back electromotive force may be due to frictional electricity, from the friction of the cathode against the liquid, or a more rapid solubility of the cathode than the anode. An increase in relative solubility of the cathode may be caused by the fact that the crystals at this electrode are much smaller than those of cast copper, or increased stirring, tending to equalize the concentration of the liquid about the cathode, and aiding diffusion, would

allow the cathode to dissolve more rapidly than the anode, and thus set up a back electromotive force. Lastly the increased relative solubility of the cathode and anode may be due to a combination of the last reason with another. There may be an impoverishment with respect to copper ions in the film about the cathode. This then would give the cell,

$$Cu \mid x - y\ Cu'' \quad xCu'' \mid Cu,$$

or a concentration cell, manifesting its electromotive force in a direction opposite the charging voltage. When, now, the cathode is rotated, the increase in solubility may be greater than the

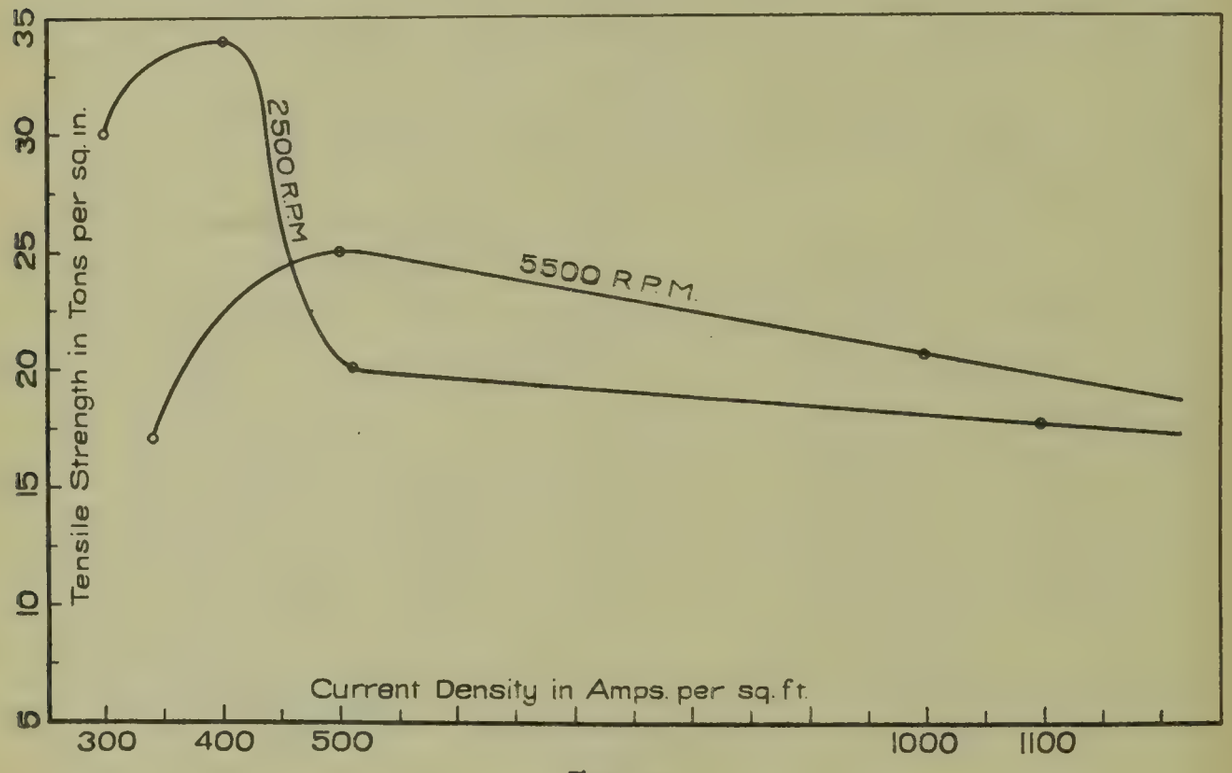

FIG. 3.

reverse tendency, caused by stirring the solution faster, and consequently the final effect would be a total increase in the solubility of the cathode, and hence a higher back electromotive force. Which and how many of these factors enter, in determining the increase in voltage, cannot be said at present. A detailed study of this, however, has been begun, and it is hoped that results will be forthcoming. This seems to be an important point in explaining some of the results gotten with revolving cathodes. These will be dealt with in detail in a future paper.

The variation of current density was then studied. It is generally known, that rapid crystallization from a solution or

"melt," gives smaller crystals, than that which takes place more slowly. If now in depositing a metal the current density be increased, the amount of metal to crystallize in unit time is increased, and hence the crystals should be smaller. With the smaller crystals goes more even loading stress and hence higher tensile strength. Therefore, for any given set of conditions the tensile strength ought to increase as the current density is increased. The upper limit will depend on the rate of stirring, other things being equal. If this be true, the maximum tensile strength would be found at a higher current density, if the stirring were more vigorous. To show this, two series of observations were made, one at 2,500 R. P. M., another at 5,500 R. P. M. These were not, however, run under the same conditions. Due to the large current used, the temperature rise was found to be different in the series of the first run. To decrease this difference a higher initial temperature was used in the second series. The effect of this increase had been anticipated, and will be discussed under temperature, below. The desired point, however, is illustrated, that is, that the maximum tensile strength is obtained at a higher current density where the rate of rotation and hence rate of stirring is higher. The solution was the same as was used before. In the first series, the initial temperature was that of the room, in the last it was about 50°C. Results are tabulated below:

2,500 Revolutions Per Minute.

Amperes per Square Foot	Amperes per Square Dm.	Voltage	Tensile Strength Pounds per Sq. In.	Tensile Strength Kilo. per Sq. Mm.
300	33	2.5	60,000	42.0
400	44	3.3	68,000	47.6
510	56	3.9	40,000	28.0
1,100	121	7.2	35,000	24.5
1,700	187	12.2	14,000	9.8

5,500 Revolutions Per Minute.

Amperes per Square Foot	Amperes per Square Dm.	Voltage	Tensile Strength Pounds per Sq. In.	Tensile Strength Kilo. per Sq. Mm.
340	37	2.7	34,000	23.8
500	55	3.8	50,000	35.0
1,000	110	7.1	41,000	28.7
1,600	176	11.1	32,000	22.4
2,400	264	20.3	28,000	19.6
4,000	440	27.5	13,000	9.1

These results are shown graphically by curves in Fig. 3.

The first three points were checked, that there might be no doubt as to the form of the curves. The tensile strength reaches a maximum and then drops off. This is due, no doubt, to the inefficient stirring, at the higher current densities. The current density was run up to a limit where the deposit was noticeably bad, due to the separation, probably, of cuprous oxide. The sample at 2,400 amperes per square foot (264 A. per sq. dm.) was very ductile, could be bent and worked nicely. No trace of oxide or other impurity was noted. The sample at 4,000 amperes per square foot (440 A. per sq. dm.) was brittle, but worked nicely in the lathe, giving a perfect copper surface. The fracture, however, showed a reddish brown color.

Upon examination under the microscope a gradual decrease in the size of the crystals with increase in current density could be noticed.

A few runs were made to show that variation of the concentration of the electrolyte makes little difference in the tensile strength. The following experiments were made, varying first the concentration of copper sulphate and then that of the sulphuric acid.

Current Density 500 Amperes per Square Foot.

(*55 Amperes per Sq. Dm.*)

Percent $CuSO_4.5H_2O$	Percent H_2SO_4	Tensile Strength: Pounds per Sq. In.	Tensile Strength: Kilo. per Sq. Mm.
12	15	60,000	42.0
20	15	58,000	40.6
25	15	55,000	38.5
15	12	60,000	42.0
15	25	57,000	39.9

The last one of each series is a bit low, but this is due to the slightly elevated initial temperature required to hold the copper sulphate in solution. The current efficiency was not so good where a large percentage of acid was used.

Now as to temperature variation, which has been anticipated above. If copper wire be drawn while cold through a die, the effect is a decrease in ductility and an increase in tensile strength. This is caused by the breaking down of the large crystals, giving smaller ones embedded more or less in amorphous material. The distance of shear through the crystal is relatively short, and

hence the elongation is short, or in other words the ductility is slight. The tensile strength goes up, for the material is worked more or less toward the amorphous end, *i. e.*, the crystals become smaller and under stress show a more even loading. If the hard drawn copper wire be annealed, the tensile strength goes down to about 30,000 pounds per square inch (21.0 kg. per sq. mm.) as a limit, and the ductility is increased. The crystals become larger, the distance of shear before they break is longer and hence the ductility is increased. By depositing copper on a rotating cathode, from a solution at room temperature, it is possible to duplicate the cold worked copper, getting a hard

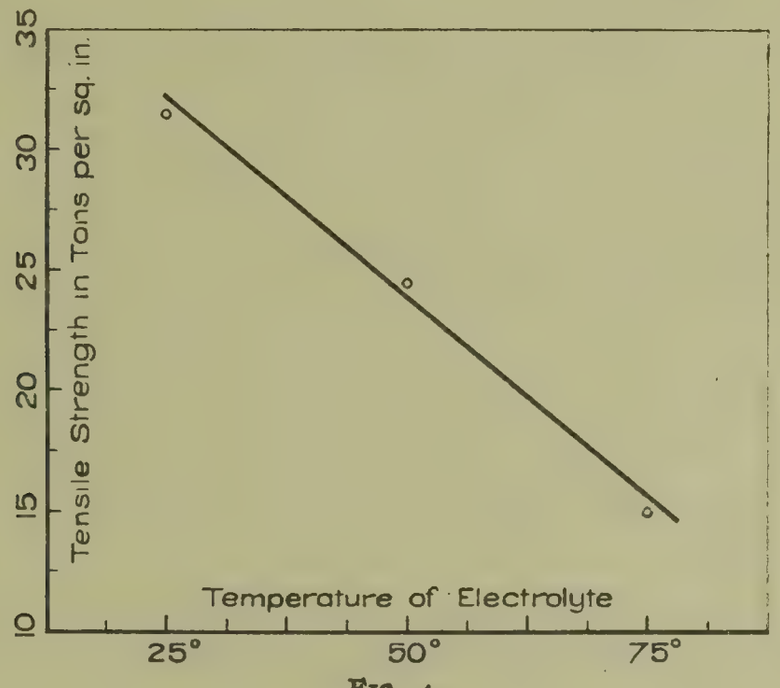

FIG. 4.

compact sample with very slight ductility, and a high tensile strength. Now by raising the temperature of the solution and hence that of the uncrystallized copper deposited, it ought to be possible to anneal the metal, while it is being precipitated. Or looked at from the other point of view, crystallization from a hotter solution should give larger crystals, other things being equal. The following illustrates the principle admirably:

Current Density 500 Amperes per Square Foot.

Temperature	Tensile Strength	
	Pounds per Sq. In.	Kilo. per Sq. Mm.
25°C.	63,000	43.1
50°C.	49,000	34.3
75°C.	30,000	21.0

This is graphically illustrated by a curve, Fig. 4. The last sample especially, was very ductile and soft, and very similar in properties to the annealed copper wire.

In this work at the current densities above 500 amperes per square foot (55 A. per sq. dm.) no attempts were made to cool the solution during the progress of the run. The large rise in temperature explains why the tensile strength at the higher current densities was always low. The heat developed by the resistance of the solution keeps the temperature up, and anneals the deposit while forming. Under these conditions the maximum tensile strength is that of soft drawn copper, 30,000 to 35,000 pounds per square inch (21 to 24.5 kg. per sq. mm.). The samples above 500 amperes per square foot (55 A. per sq. dm.) Fig. 3, were all ductile except the last ones of the two series, given at 2,500 and 5,500 R. P. M. respectively. Here the deposit was noticeably bad.

It was thought advisable to get an approximation of the current efficiency with the rotating cathode at a high current density. There being no evolution of gas at either electrode this was gotten by taking the ratio of the anode loss and cathode gain. Consequently, a run was made, using 1,000 amperes per square foot (110 A. per sq. dm.) while the cathode was rotated 5,500 R. P.M. The results follow:

Weight of Anodes before.....2,582 grams
Weight of Anodes after.....2,529 grams

Anodes loss .....53.0 grams

Weight of Cathode after..... 869 grams
Weight of Cathode before..... 816.2 grams

Cathode gain .....52.8 grams

$$\frac{52.8}{53} = 99.6 \text{ Current Efficiency.}$$

The efficiency therefore is practically 100 percent.

Some runs were made with varying amounts of gelatine (½ to 5 grams per liter of solution) to see if the character of the deposit would be improved. Good conditions otherwise, that is, 400 amperes per square foot (44 A. per sq. dm.) at 2,500 R. P. M., were used. The deposits, however, were very hard, and so brittle they could be crushed between the fingers. The

brittleness was no doubt due to the mechanical deposition of traces of gelatine, with the copper. The gelatine is undoubtedly present here as a colloid. It is possible that the particles of copper become covered with a surface film of the gelatine, and are thus prevented from adhering to each other. Thus a "brick and mortar" structure would result, which could easily be broken down. This is of importance in accounting for the results gotten with bronze, for here too, there is certainly colloidal tin oxide present in the solution.

A run was made with copper nitrate and nitric acid, the concentrations of which were equivalent to 15 percent $CuSO_4.5H_2O$ and 12 percent H_2SO_4. A current density of 500 amperes per square foot (55 A. per sq. dm.) at 2,500 R. P. M. was used. The deposit, however, was dark, hard, and brittle.

In an attempt to apply the principle of rapid stirring and high current density, to the alloys of copper, bronze was studied. The first question was that of a solution from which to deposit the copper and tin. The solution recommended by Curry[8] was first tried. The solution contained 15 grams of $CuSO_4.5H_2O$, 28 grams of SnC_2O_4, 5 grams of $H_2C_2O_4$, and 55 grams of $(NH_4)_2C_2O_4$ per liter of water. The anodes were 90 percent copper and 10 percent tin. The current density varied from 20 to 200 amperes per square foot (2.2 to 22 A. per sq. dm.), but no satisfactory deposit could be obtained. At first bronze would be deposited, then the deposit became rich in copper until finally only copper was precipitated. $CuCl_2.2H_2O$ was substituted for $CuSO_4.5H_2O$ with only greater complications, for here we introduced the possibility of cuprous chloride. The conductivity of the solution was increased by adding ammonium chloride, but the character of the deposit was not enhanced.

There are two possibilities here. The tin may go in as stannous tin and be oxidized to the stannic condition, from which it would not be precipitated, or the tin may dissolve and become colloidal. If the latter be true, a copper-rich deposit should be obtained from the beginning, if the solution were boiled before the deposition was started. Here the tin in solution would be changed entirely to the colloidal state, and only copper would deposit. When this was tried the results indicated that the tin went bad

[8] Jour. Phys. Chem. **10**, 515 (1906).

due to the formation of the colloid. A solution was made up as given above. One portion was electrolyzed cold for a minute, and another, after being boiled, was run under identical conditions. A bronze was obtained in the first case, while in the latter practically a pure deposit of copper resulted.

On account of the low conductivity of this solution it was deemed wiser to study the alkaline tartrate for use in this precipitation. When the solution recommended[9] was tried, no deposit at all could be obtained. The sodium hydroxide concentration was high enough so that presumably it alone was decomposed. Some preliminary runs were made then, on a small scale, to determine the proper concentration of the various substances. Solutions containing copper sulphate and sodium stannate in the proportion of 90 parts of copper to 10 parts of tin, with enough sodium potassium tartrate to dissolve the whole easily, with varying amounts of sodium hydroxide, were electrolyzed with an anode of 90 percent copper, and 10 percent tin. These were run at a moderate current density, using a rotating perforated platinum electrode. After running for at least twenty-four hours and after a deposit of constant composition was obtained, the deposits were compared, the solution giving the best bronze was analyzed, and this concentration used. This solution contained 22 grams of $CuSO_4.5H_2O$, 5.5 grams of Na_2SnO_3, 150 grams of $NaKC_4H_4O_6$, and 5 grams of NaOH per liter. The anode analyzed 89 percent copper, the cathode 93.5 percent copper. From this and a consideration of the final tin content, a good part of the tin went into the electrolyte in the unavailable form, most likely colloidal. The deposit on the platinum was brittle. However, about 50 grams of a compact deposit was obtained, which showed very nearly the same composition throughout. The solution above being used, runs were made with 6, 18, and 30 amperes per square foot (0.7, 2.0 and 3.3 A. per sq. dm.), but the deposits were too brittle to get a measurement of the tensile strength. The relative amounts being the same, the solution was made five times more concentrated, in order to increase the conductivity, and runs were made at 150 and 250 amperes per square foot (16.5 and 27.5 A. per sq. dm.). The deposits were no better, however. The trouble here is most likely due

[9] McMillan, A Treatise on Electro-Metallurgy, p. 287.

to the colloidal material. This may be mechanically deposited with the bronze and prevent adherence, as the gelatine with the copper. Colloidal tin or tin oxide is no doubt present, for the tin content in the solution gradually goes up, showing that it is going into solution in an unavailable form. Tests applied for stannic tin were negative. When this is taken up again, the question of a solution is the first one to be answered. A systematic search should be made for a solution of high conductivity, where the chances for the formation of colloidal material and stannic tin are negligible, and for one, from which a deposit of constant composition can be gotten. Any attempt to use the solution given above is useless if a bronze with good physical properties is desired.

The next attempts at the application of the foregoing principle of rapid stirring and high current density, were the study of brass. The solution used here was one of the double cyanides of copper and zinc with excess of potassium cyanide. This solution, 85 grams of $ZnSO_4.7H_2O$, 35 grams of $Cu(CN)_2$, and 130 grams of KCN per liter, was electrolyzed with brass anodes containing 60 percent copper and 40 percent zinc. The current density varied from 12 to 150 amperes per square foot (1.3 to 16.5 A. per sq. dm.), with a rotation of 2,500 R. P. M. Only one deposit was tough enough to test. A measurement was obtained on the run at 75 amperes per square foot (8.25 A. per sq. dm.). The average of two tests gave 9,500 pounds per square inch (6.65 kg. per sq. mm.). Two pieces were annealed at 800°C. for eight hours and quenched, and then tested. Curiously the tensile strength went up. The average of two measurements gave 18,000 pounds per square inch (12.6 kg. per sq. mm.). There had been a change in the piece other than the growth of the crystals, otherwise the tensile strength would have gone down. The fracture of the unannealed piece was interspersed with brownish black specks and lines which disappeared when the piece was annealed. It is possible that the piece as deposited had interspersed through it, probably as a film around the crystals, some decomposition product of the cyanide solution, which was driven out by annealing at the temperature used. At least, the curious reversal must have been due to the freakishness of the unannealed piece, since its tensile strength was very much

too low for unannealed alpha brass. A sample was also heated to redness by passing an electric current through it. The tensile strength was increased, as when the piece was annealed. The disturbing film around the metal was most likely burned out.

Some runs were made with anodes, well over in the alpha field, 70 percent copper and 30 percent zinc, with more rapid stirring, but the deposit was very brittle. In practically all runs with brass, the first thin film of the deposit was very good. It was foil that could be bent into any shape. This was not tested because the results would have meant nothing, since the deposition could not be carried on indefinitely. The solution must change soon after the electrolysis is started. What this change is, or how it is brought about, is not known.

What was said of the bronzing solution applies also to those for brass plating. For this high current density work, it seems that an acid solution with very soluble salts of the metals will have to be found. While these experiments on the alloys have not been satisfactory in any respect, they at least point out some lines along which work would be fruitless.

Conclusion.

These experiments have shown that,

1. Copper has been deposited electrolytically at a current density of 4,000 amperes per square foot or about 430 amperes per square decimeter.

2. In the electrolytic precipitation of a metal the crystal size decreases as the cathode is rotated more rapidly, other things being equal.

3. The crystal size decreases as the current density increases, and increases as the temperature rises.

4. The concentration of the electrolyte can be varied quite a little without changing the character of the deposit.

5. If the precipitation is carried on at a high temperature an effect similar to annealing is accomplished during the electrolysis.

6. The tensile strength of metals varies inversely as the crystal size, and hence any factor tending to decrease the crystal size tends to increase the tensile strength.

7. The effect of rapidly rotating the cathode and of increasing the current density is to increase the tensile strength, the crystal size being decreased.

8. A good deposit of copper could apparently be obtained at an infinite current density if the stirring were efficient enough to prevent impoverishment.

9. The current efficiency at a high current density with rapid rate of rotation, is high, it being 99.6 percent.

10. "Hard drawn" copper can be deposited on a rotating cathode at almost any current density, if the temperature be kept down; and likewise annealed copper, if the temperature be kept at about 75°C.

11. Electrolytic copper has been obtained having a tensile strength of 68,000 pounds per square inch (47.6 kg. per sq. mm.).

12. A deposit as good as the best can be obtained with a current density of 2,400 amperes or more per square foot (264 A. per sq. dm.) with the rate of stirring used.

13. With the alloys, the trouble is most likely a question of colloidal material.

14. Acid solutions, with readily soluble salts, and no possibility for the formation of colloids should be sought for as electrolytes in alloy precipitation.

This work was suggested by Professor Bancroft and carried out under his supervision, to whom, with Professor Upton, of Sibley College, I wish to express my sincere thanks for advice and suggestions. Thanks are also due to Sibley College for co-operation by giving me the use of apparatus and machine shops.

Cornell University,
Ithaca, N. Y.

DISCUSSION.

DR. CARL HERING: It seems to me that what was really sought was to get a high surface velocity between the cathode and the liquid, and it seems that the chief difficulties lie in

running a machine at 6,000 r. p. m. I would therefore suggest that if the cathode cylinder be made 2 in. (5 cm.) diameter, instead of 1 in. (2.5 cm.), the revolutions could be reduced to 3,000, or with a 3 in. (7.5 cm.) cylinder the speed would be only 2,000 r. p. m. This reduction of speed would diminish much of the trouble which was apparently encountered. Hence it seems to me that the results shown in these curves might have been better given in terms of the surface velocity, instead of in revolutions per minute. Similarly good deposits have been obtained by moving the liquid instead of the cathode. I remember reading about some experiments many years ago in which the liquid was squirted up against the cathode; enormous current densities were used and yet the deposits were very good.

PRESIDENT WHITNEY: I understand that this is annealed copper. How did the crystals look?

MR. C. W. BENNETT: Measurements of the actual cross section of the crystals were desired, but the crystals were so very small and their boundaries so indistinct that the measurements would not have meant much had they been taken. A difference of cross section was, however, apparent to the eye when the samples were successively brought under the microscope.

With reference to Mr. Hering's suggestion in regard to the surface velocity of rotation, it may be said that equal surface velocities would appear, on first glance, to give the same effect. With the same surface speed the same agitation of the liquid per unit area would be obtained. Since the stirring is the same per unit area, and there is twice the area with the larger cathode as with the smaller, it will necessarily take twice the power to rotate the larger cathode at one-half the speed of the smaller one. While no experiments have been made along this line, this must be the case, else with a larger cathode surface the current used and hence the metal deposited could be increased without an increase in the power required for stirring.

It must be remembered, however, that this cathode is a laboratory instrument. To obtain, therefore, the same amount of stirring and to use the same current density, with the larger cathode, the construction would have to be more rugged, the power required for rotation double, and the current for the

electrolysis double. With the present arrangement to obtain test samples of the proper length at a current density of 4,000 amperes per square foot, 300 amperes was used for the electrolysis. With the larger cathode 600 amperes would have been required. Then too, more metal was obtained than necessary for the tests. With the larger cathode, of course, twice the amount of metal would have been obtained. The reasons, therefore, for constructing the cathode of the size given, for laboratory work, are evident.

MR. HENRY D. HIBBARD: If I read the last diagram rightly, it shows that a considerable part of the tensile strength was eliminated by raising the temperature of the electrolyte from 25 to 75 degrees, is that right? I would like to know how that is explained.

MR. BENNETT: That is not extraordinary when it is considered that cold-worked copper has a tensile strength of about 70,000 pounds per square inch, which, when the copper is annealed, drops to about 30,000 pounds per square inch as a limit. By depositing the copper at a high temperature, the effect of annealing is obtained. Copper may be annealed by heating at definite temperatures, these temperatures depending on the time of annealing. In other words, the same effect may be obtained by heating at a low temperature for a long time, as is obtained by heating for a short time at a high temperature.

MR. HIBBARD: As low as 75 degrees?

MR. BENNETT: Copper can be annealed at 125 degrees. It must be remembered, however, that there are two factors in the so-called electrolytic annealing: First, the question of chemical crystallization from the uncrystallized copper, and second, the question of the growth of the crystals of the metal from the already crystalline mass. The former of these factors, of course, is the important one.

MR. HIBBARD: If that curve was continued to a temperature of zero, what would be its form?

MR. BENNETT: The question arose as to what type of curve should be drawn between the three points on the temperature-tensile strength curve, Fig. 3. A straight line was drawn. As

to the extension of the curve for higher temperatures, it would probably become parallel to the axis, giving a tensile strength corresponding to the limiting value for annealed copper.

MR. HIBBARD: What at the other end, the zero end?

MR. BENNETT: No experiments were made on cooling the liquid. It will be very interesting to determine these factors at lower temperatures, and as the work with the rotating cathode is to be carried on further, it is hoped that such measurements may be obtained. As to the actual tensile strength at lower temperatures, it is safe to assume that a limiting value, corresponding to that of cold worked copper, would be obtained.

Without cooling the solution, where the current was 300, corresponding to 4,000 amperes per square foot (4.4 A. per sq. dm.), it took only about two minutes to bring the solution of 12 percent acid and 12 percent copper sulphate, from room temperature, up to the boiling point. It is anticipated, therefore, that the cooling system will introduce difficulties.

MR. HIBBARD: This recalls some work done twenty-five years ago by a man named Elmore. There had been a bad marine accident, due to a burst steam pipe which burst at the brazed joint, and he developed means of making seamless copper tubes by electric deposition. He revolved his cathode, while precipitation was going on, and with a burnisher he burnished the metal as it was deposited. I do not know whether that process has continued in use or not.

DR. W. D. BANCROFT: It is a perfectly well-known phenomenon in the crystallization of solutions that, other things being the same, you get larger crystals at a higher temperature. It is also a well-known phenomenon that you get coarser crystals when you precipitate a metal electrolytically at a higher temperature. This is another application of the same thing; instead of measuring the crystals directly, we measure them by their tensile strength.

As regards the limiting case, there can be no question, that at the lower temperature there must come a limiting value corresponding to the limiting value obtained for a very small, hard-drawn copper wire. Precipitation at low temperatures is equivalent to hard-drawn copper. The curve unquestionably must

become parallel with the axis of abscissas, or practically parallel, both at high temperature and at low temperature, but we have no data as to that.

MR. E. B. SPEAR: Has this copper the same degree of purity at the higher temperature? I believe Prof. Bancroft pointed out some years ago in one of his works on this subject that oxides are often deposited by the effect of the high temperature.

DR. BANCROFT: The copper contains practically no oxide, except at the higher current densities.

MR. BENNETT: While no analyses of these samples were made, the physical tests gave pretty certain evidence that the metal was pure and of high grade. If oxide be present, the ductility drops off very rapidly. These samples, prepared at high temperatures, are very ductile, showing that they are pure. The samples prepared at a current density of 4,000 amperes per square foot are brittle, and upon breaking show a reddish brown surface. There is little doubt that the brittleness is due to the presence of cuprous oxide, disseminated throughout the mass.

MR. C. G. SCHLUEDERBERG: Referring to what Dr. Hering spoke of, regarding the effect of surface velocity on deposition, that same experiment has been made by plating a rapidly rotating cone at a high current density. The point of the cone contained copper which was quite crystalline, while toward the base of the cone the deposit of copper was very smooth and coherent in structure. I think this bears out the idea that the surface velocity of the rotating cathode has everything to do with the structure of the deposited copper.

MR. BENNETT: This is probably a question of impoverishment of the solution at the tip of the cone. The liquid at the tip is not stirred as it is near the base of the cone. The stirring being less at the tip of the cone, assuming equal distribution of the current, impoverishment of the lower layer would cause the deposit to go bad.

MR. C. W. BENNETT (*Communicated*): It must be remembered that in this preparation of copper there are several factors to be reckoned with. There is the question of current density,

which, of course, must necessarily be connected with the rate of stirring. Bound up with this rate of stirring is also another factor, varying simultaneously in the same direction. This factor is that of the mechanical burnishing effect, by the friction of the solution against the deposited metal. This is equivalent to working the metal at the temperature of the bath, tending, of course, to decrease the size of the crystals. At the higher rate of stirring a higher current density may be used. This gives more metal to crystallize in unit time, and, therefore, a higher rate of crystallization. This more rapid crystallization gives smaller crystals. These two factors, therefore, can be utilized in unison for the production of smaller crystals and hence metal of higher tensile strength, other things being equal. The third factor is the very important one of temperature, temperature operating according to the perfectly general laws of crystallization from solution, with which all chemists are familiar. It is believed that all the facts obtained can be readily explained by the application of known laws. These facts represent therefore, another instance of a duplication, by electrochemical methods, of the processes carried out on metals every day by other methods.

A report of progress presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

STANDARD METHODS RECOMMENDED FOR TESTING OF DRY CELLS.

A Report of Progress by the Committee on Dry Cell Tests.

This report is presented as a tentative one, subject to such revision as may be indicated as desirable by the American Electrochemical Society and by the members of this Committee. The Committee urgently requests that a full discussion be given, as the Committee feels the necessity of securing all the assistance possible in getting this report into a final and acceptable form.

When the American Electrochemical Society voted that a Committee be appointed to formulate standard methods of testing dry cells there were, apparently, among the voters those who held an impression that the task was not a difficult one and that tests could be devised which for simplicity and convenience would be comparable to the simplicity, modest proportions and values of the dry cell itself. The difficulties, however, will be as apparent to others as they have been to the Committee, when considering the various factors which must necessarily be taken into account.

The methods of testing must in the first place be of benefit to those interested in dry cells, and the users may be divided into three classes: The average ultimate consumer, the large user, and the manufacturer.

No standard methods of testing have been devised, or, we believe, can be devised, which will be suitable at once for all of these classes, and the most serious obstacles are encountered in formulating methods suitable to the first class. This is unfortunate, since by far the larger proportion of the dry cell output is so distributed that the user is interested in one, two, six, or perhaps twelve cells as supplying his yearly requirements. This very large number of users should have a test the cost and

labor of conducting which should not be out of proportion to the low values of the articles tested. There appears to be no adequate means of meeting this urgent demand for simplicity of equipment and method.[1]

The fact that there is no "X-ray" method of examining a cell to see how much energy it contains, involves the alternative method of destroying the cell to determine its energy content, and this becomes of serious moment to the ultimate consumer class. In fact, insofar as the user is concerned, your Committee must agree with Dr. Baekeland, who says that "the test for the dry cell is to use it for a particular purpose."

The large users of dry cells, such as telephone exchanges, engine manufacturers, installers of alarm and signal devices, railroads, etc., who purchase cells in large quantities, are especially interested in testing methods. Various methods of testing have been evolved by these users as a basis for purchase specifications and as a means of judging the relative merits of the various makes of cells on the market. To them the matter of elaborateness of tests is of *less* importance than to the small user.

Of even greater importance is the testing of dry cells by the manufacturer, who must necessarily adopt methods which will give him the necessary information concerning his product, no matter how elaborate.

The methods of testing which the Committee is recommending are those which are particularly suited to the second class—the large users. These tests, if extensively adopted, will be of indirect benefit to the small consumer, and will be of mutual advantage to the large users and manufacturers.

The construction of dry cells, methods of manufacture, characteristics, properties, various uses, and methods of testing are discussed in various papers presented during the past four years before the American Electrochemical Society, and these papers constitute the most important literature, at least in this country, dealing with the dry cell.

Uses of Dry Cells for Ignition Service. J. W. Brown, Transactions, **13**, 173 (1908).

Certain Characteristics of Dry Cells. C. F. Burgess and C. Hambuechen, **16**, 97 (1909).

[1] Trans. Amer. Electrochem. Soc., **17**, 365; **19**, 32.

Dry Cell Tests. F. H. Loveridge. **16**, 109 (1909).

Some Characteristics of the Modern Dry Cell. D. L. Ordway, **17**, 341 (1910).

Dry Cell Testing. W. B. Pritz, **19**, 31 (1911).

It has been suggested to this Committee that the methods for testing should include, aside from electrical measurement, methods of physical and chemical analysis, such that judgment may be made thereby of the merits of a cell, and that what constitutes a satisfactory product should be described in these terms so that they might form a basis of specification. There is a striking similarity between the various cells on the market as far as materials used and general structure are concerned. Exceedingly slight variations, however, which introduce large variations in the quality of the product, are not capable of detection by physical and chemical examination, and what is of even greater importance in determining the quality are the methods of assembling, such as methods of mixing, grading as to size of the particles which constitute the cell mixture, and methods of tamping, factors which cannot be easily determined by physical or chemical inspection of the resultant product.

The art of dry cell manufacture cannot be considered as having been worked out to a finality; improvements are being made and will continue to be made. One maker may discover a simple method of neutralizing the effects of an impurity on his product which may have a detrimental influence in another product, and a judgment based upon the detection of such impurity would thereby work an injustice. The tests, therefore, should be such as determine the ability of the cell *to produce results*, and these can be determined only by tests involving electrical measurement. The dry cell, in all of its multitudinous uses, is merely a source of electrical energy, and its ability to deliver this energy, in the quantity and at the times desired, constitutes the principal measure of value.

Dry cell tests may be conveniently divided into three main groups, viz.:

I. Tests to determine whether or not a cell is in good condition before being placed in service.

II. Tests to determine the actual or comparative service capacity of cells.

III. Tests to determine the rate of deterioration of cells on open circuit.

This classification is followed in this report. Long discussions of the points brought out have been avoided as much as possible, references to the literature where such discussions may be found being given instead.

TESTS TO DETERMINE THE CONDITION OF A CELL BEFORE USE.

I. Electromotive Force:[2]—The electromotive force of a cell may be read by connecting a voltmeter directly across the terminals.

Notes:—In new cells of various types the electromotive force may vary from 1.5 to 1.6 volts. If a cell of the type now in general use gives an E.M.F. five or more hundredths less than 1.5 volts it is an almost certain indication either of serious deterioration due to age, or of the external short-circuiting of the cell, or of some defect such as an internal short-circuit, which will soon render the cell unfit for service.

It is seldom necessary to measure the open circuit voltage of cells, since they are seldom deficient in this respect. It is a test which may be considered as secondary in nature, and should be applied when it is suspected that the cells are below standard, for example, when cells are received with wet jackets, when the terminals are corroded, when the electrolyte leaks from under the seal, or when the cells are abnormally low in short-circuit current.

An accurate or carefully calibrated voltmeter should be used, the resistance of which is sufficiently high to render the current flow through it inappreciable. A two-scale Weston instrument of 300 ohms resistance with 3-volt maximum deflection and 1,500 ohms with 15 volts maximum deflection has been found very satisfactory for both cells and batteries. Cheap pocket instruments are often so inaccurate as to make their indications of open circuit voltage worse than useless.

The effect of temperature on electromotive force is very slight, amounting to only a few hundredths of a volt between all ordinary

[2] Trans. Amer. Electrochem. Soc., **16**, 103 (1909); **17**, 345 (1910).

temperature ranges. The voltage returns to normal with the temperature.

II. Short-circuit Current:—The short-circuit current of a cell may be obtained by connecting an ammeter directly across the terminals of the cell.

Notes:—The short-circuit current of a cell is of value only when coupled with a familiarity with the brand of cell in question. If the reading is normal for that brand of cell, it is reasonably certain that the particular cell is in good condition, and that it will probably give as good service as others of the same make. This applies only to cells of the same brand and make. That the short-circuit current of a cell of a new and unfamiliar brand is as high as that of another brand is no indication whatever of the equality of the service capacities of the two cells.[3] The short-circuit current bears no relationship to service, and when measured without reference to temperature or other conditions may be entirely meaningless and misleading.

The ammeter for reading short-circuit current should be dead-beat, and with its leads should have a resistance of 0.01 ohm, to within 0.002 ohm. Two 30-inch lengths of No. 12 lamp-cord make very convenient leads. The maximum swing of the needle should be taken as the short-circuit current of the cell.

The ammeter should be connected across the brass terminals of the electrodes. Low readings are apt to be obtained if the ammeter is applied to the carbon electrode directly.

In order to avoid high contact resistance, the terminals of the cells and of the ammeter leads should be brightened. It has been found very convenient to fit the ammeter leads with small terminals of lead. The contact on the cell terminals is greatly improved, and with such leads it is unnecessary to brighten the contacts.

For accurate measurement of the short-circuit current of a new cell, cheap instruments of the pocket type should be avoided.[4]

The effect of temperature on the short-circuit current[5] is quite pronounced. Between 10 and 80 degrees centigrade, the amper-

[3] Trans. Amer. Electrochem. Soc., **13**, 178 (1908); **16**, 110 (1909); **17**, 346 (1910); **19**, 33 (1911).

[4] Trans. Amer. Electrochem. Soc., **16**, 117 (1909).

[5] Trans. Amer. Electrochem. Soc., **17**, 356 (1910); **19**, 37 (1911).

age of cells is raised on an average of about 1 ampere for each 10 degrees centigrade rise in temperature. This value varies considerably with different cells, and is somewhat greater at the lower (colder) end of the scale and less at the higher. At very low temperatures the effect is very pronounced, and it is often noted that cells received in extremely cold weather read but one or two amperes. On bringing them to room temperatures, however, the short-circuit current becomes normal and the cell is not impaired by the freezing.

III. Internal Resistance:[6]—This value is usually determined by applying the formula—

$$\text{Int. Res.} = \frac{V - V'}{C}$$

where V is the open circuit voltage of the cell, V' the closed circuit voltage, and C the current drain to which the cell is subjected in order to make the determination.

Notes.—The above formula gives a compound value, composed partly of the sum of the resistances of the various parts of the cell, and partly of the resultant of the various electromotive forces in operation during the action of the cell. The value obtained varies with the current flowing, the age of the cell, and the temperature.

For these reasons we advise against the use of this test. It indicates nothing in regard to the service capacity, nor does it give an exact value of the actual internal resistance of the cell.

SERVICE CAPACITY TESTS—GENERAL DISCUSSION.

Requirements for a satisfactory test:—In general there are but two reasons for desiring a service test upon dry cells:

1. To ascertain what life may be obtained from a brand of cells in a certain service.

2. To ascertain which one of several brands will give the longest life in that particular service.

With the former object in view the knowledge is best obtained by actual use of the cells in connection with the appliance. In some

[6] Trans. Amer. Electrochem. Soc., 17, 348 (1910).

cases this is the only feasible way in which the definite information sought can be obtained. The great majority of tests are carried on, however, with the second object in view, viz., the comparison of two or more brands of cells for use in a particular service. Where the amount of testing is large, it is impossible, even were it expedient, to use the actual appliances for testing cells, and it becomes necessary to devise special testing methods and apparatus such that results obtained therefrom shall be comparable to the results obtained from the cells when placed in actual service. This is, we take it, the one necessary condition which dry cell tests must fulfil.

There have been tests devised which seek to go further and make the operating conditions not only comparable, but as similar as may be to the operating conditions of the service for which the test is intended. Upon this point there is some diversity of opinion. Some authorities claim that a test is of greater value and is more reliable the more nearly the conditions of test approach those of service, and, following out these claims, have devised certain tests which are rendered quite complicated, requiring much attention and apparatus for their continuance, by the introduction into the method of some of the irregularities to be expected in service. It is questionable, however, if results of greater meaning are obtained from such strict adherence to service conditions. At best, such a test is but an approach to actual service, which must be continually varying from time to time and from locality to locality. Again, the apparatus necessary to carry on an irregular, intermittent test is very complicated and requires much careful attention. This feature limits its use to the large consumers and manufacturers.

Testing cells in series:—It has been suggested that cells of various makes be tested by connecting them in series and discharging them simultaneously through any suitable resistance, thereby assuring that the cells are discharged at the same rate and under identical conditions. There are several objections to this method[7] and we therefore advise against the testing of cells in this manner.

Judging Results:—In interpreting the results obtained from a test of various grades of cells, we wish to caution against

[7] Trans. Amer. Electrochem. Soc., 19, 36 (1911).

drawing definite conclusions from the outcome of a single test or of a small number of tests. When the matter of choosing a brand is of much importance, it is necessary to run a series of tests over a period of six months or a year. In this way a very good idea may be obtained of the average service results which may be expected.

In the following table are given the results of ten monthly tests completed during 1910 on two brands of dry cells. The values represent the length of service given:

Tests	1	2	3	4	5	6	7	8	9	10	Average
Brand A....	42	35	38	33	60	45	48	35	66	48	45.0
Brand B....	30	37	24	25	27	40	48	42	40	40	35.3

It is very evident from a comparison of the averages of these tests that Brand A is much superior to Brand B, yet had the consumer only the results from tests 2 or 8, he would have undoubtedly arrived at a very erroneous conclusion regarding the real merits of the two brands.

SERVICE TESTS RECOMMENDED.

I. Telephone Service:[8]—Discharge three cells, connected in series, through 20 ohms resistance for a period of two minutes, each hour, during 24 hours per day and seven days per week, until the closed circuit voltage of the battery at the end of a period of contact falls to 2.8 volts.

The following readings are taken:

1. Initial open circuit voltage of the battery.
2. Initial closed circuit voltage of the battery.
3. Closed circuit voltage at the end of the first discharged period.
4. Closed circuit voltage at the end of a discharged period after three days, and weekly thereafter.

Report the results as the number of days during which the closed circuit voltage remains above the limiting value of 2.8 volts.

Notes:—Fig. 1 shows in diagrammatic form a very convenient and inexpensive method of carrying on this test.

[8] Trans. Amer. Electrochem. Soc., **17**, 358 (1910); **19**, 41 (1911).

The left hand portion indicates the apparatus necessary and its arrangement. The hand of the clock A revolves once per hour, closing, by means of a suitable contact H, the circuit of the battery I in turn through the contacts B_1, B_2, B_3 and B_4, on the face of the clock. This current magnetizes in turn the cores of the relays C_1, C_2, C_3 and C_4, causing the extended armature arms D to fall, bringing the inverted U shaped fingers F into mercury cups, to which the terminals of the individual test circuits are connected. Each contact plate B is of such length that two minutes are required for the passage of the contact H.

At the right of the figure is shown one testing unit, consisting of the relay C, the mercury cups into which dip the contact

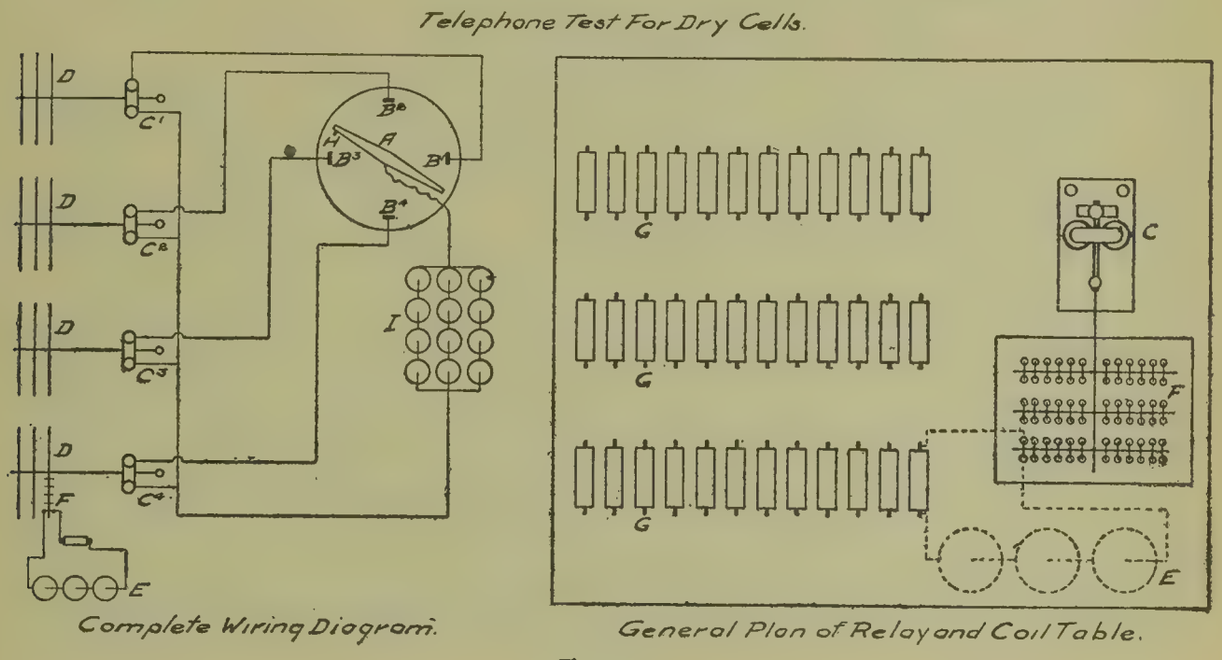

FIG. 1.

fingers F, and the arrangement of the 20-ohm resistance coils G.

The batteries E, are stored under the table on which the various parts are fixed. One complete test battery circuit is indicated by the dotted lines.

Fig. 2 shows a representative discharge curve obtained from a battery of three 2½ x 6 inch (6 x 15 cm.) cells of a well known brand. The curve passes through the values of the closed circuit voltage at the ends of the contact periods.

The test should be conducted in a dry place, and normal room temperature should be maintained as closely as possible.

II. Ignition Service:—Discharge six cells connected in series through 16 ohms resistance for two periods of one hour each

per day, seven days per week. The periods should be eleven hours apart, but in cases where the circuits are not automatically controlled, the first and the last hour in the working day may be chosen for the discharge periods and the discharge omitted on Sunday, without materially affecting the results.

The following readings are taken:

1. The initial open circuit voltage and short-circuit current of the battery.

2. The initial closed circuit or working voltage, and the initial impulse of current which the battery is capable of forcing through a 0.5-ohm coil connected in series with an ammeter, and in parallel with the 16-ohm coil.

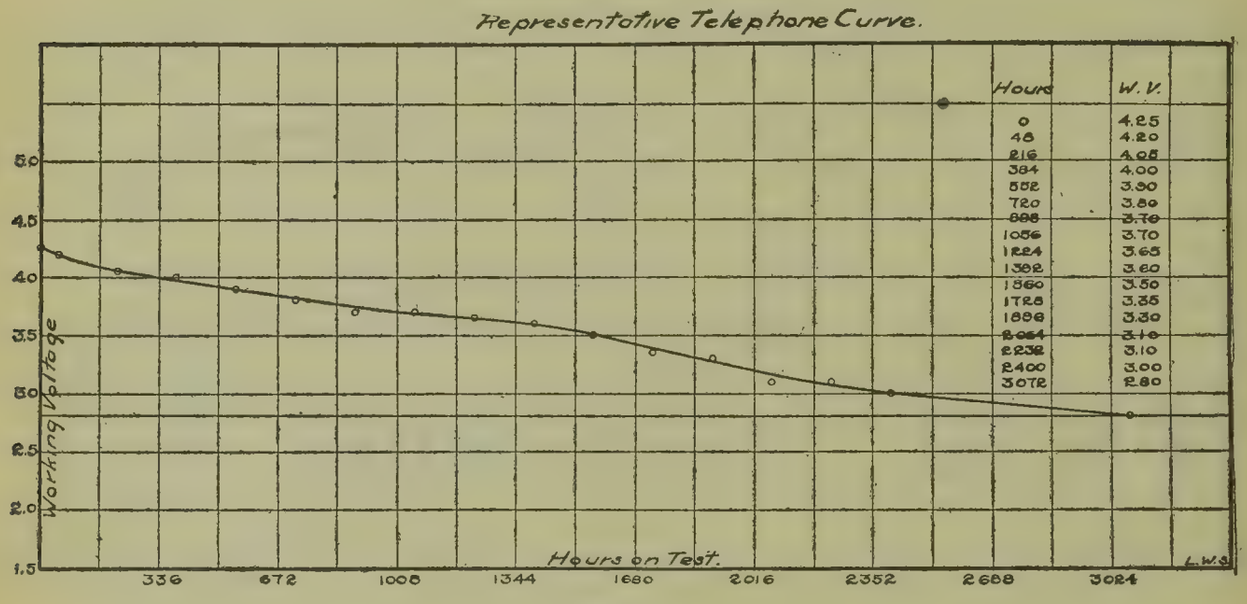

FIG. 2.

3. Closed circuit voltage and impulse current through the 0.5-ohm coil at the end of the first period of closure, at the end of the sixth period, at the end of the twelfth period, and after every twelfth period thereafter.

The test is considered completed when the impulse current at the end of a period falls below four amperes. Report the results as the number of hours of actual discharge to the limiting value of impulse current.

Notes:—Fig. 3 shows diagrammatically the arrangement for a single test.

When the number of tests is not large the circuits may easily be closed by hand. When a great many tests are to be made,

it is convenient to arrange a clock-operated automatic circuit closing device.

By varying the length or number of discharge periods, the test may be made representative of any special cases of ignition. For a good comparison of the fitness of various cells for general ignition service however, the test as given above is to be recommended.

Particular care should be taken to keep the temperature of ignition test batteries as nearly constant as possible, as the service obtainable is greatly influenced by this factor, as shown by the following table in which are given the averages of five separate

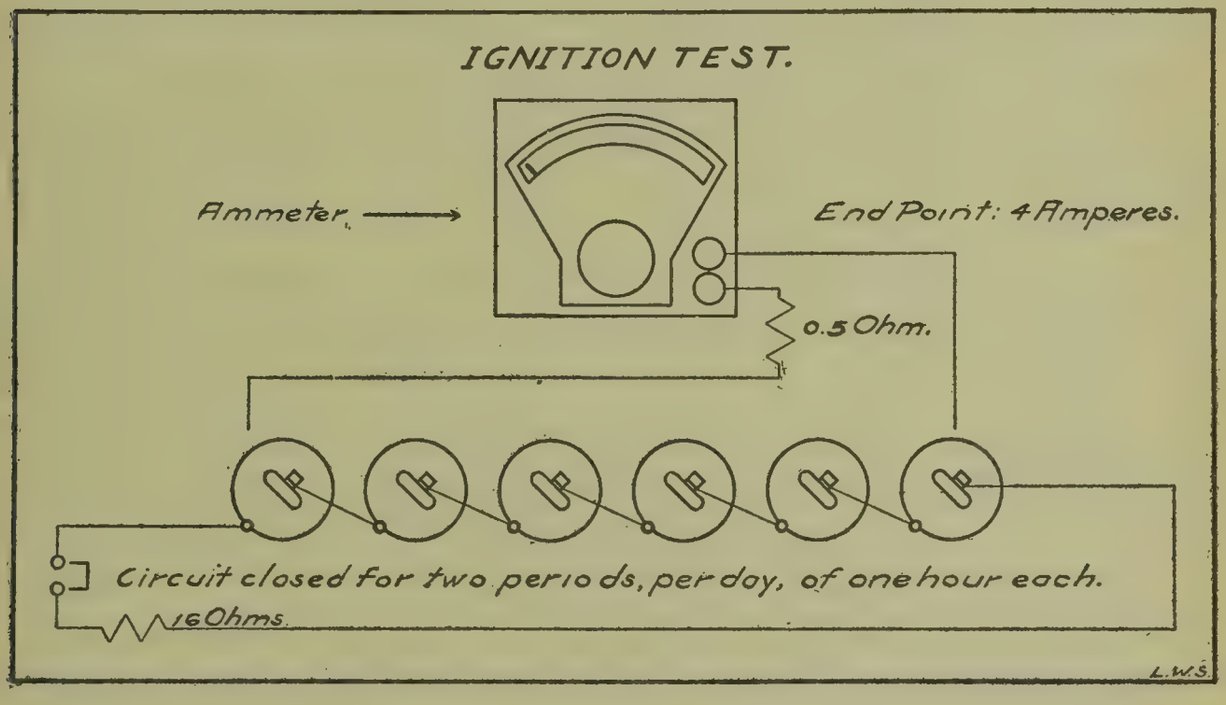

FIG. 3.

tests conducted at 5, 25, 35, 45, 55, 65, and 75 degrees centigrade.

Temperature	5°	25°	35°	45°	55°	65°	75°
Hours service	31.9	46.3	50.4	46.2	35.6	29.3	26.6

The reasons for the adoption of the various constants of this test, viz., number of cells, resistance in main circuit, end point, and resistance in ammeter circuit, is fully described in the Trans. Amer. Electrochem. Soc. **13**, 178 (1908); **17**, 361 (1910), **19**, 43 (1911).

III. Flash-light Batteries:—Discharge the battery to be tested through a resistance of four ohms for every cell in series, viz.,

eight ohms for a two-cell battery and 12 ohms for a three-cell battery, for a period of five minutes once each day until the closed circuit voltage at the end of a discharge period falls to 0.75 volt per cell, viz., 1.5 volts for a two-cell and 2.25 volts for a three-cell battery.

The following readings are taken:

1. Initial open-circuit voltage and short-circuit current.

2. Initial closed-circuit, or working voltage.

3. Closed-circuit voltage at the end of the first, third and seventh periods of closure, and after each seventh period thereafter.

Report the results as the number of minutes during which the battery was discharged through the resistance to the given end point.

Notes:—In case the circuits are not operated mechanically, the results are not materially changed if the batteries are discharged only on working days.

Four ohms per cell is chosen for the resistance in circuit, since the tungsten bulbs generally used with a three-cell battery have a resistance of approximately 12 ohms.

Miscellaneous Services:—In addition to the telephone and ignition services, which are by far the most important services in which dry cells are used, there are numerous other services, among which may be mentioned the operation of automobile horns, sewing machine motors, small fans, toys, massage vibrators, cigar lighters, bells, buzzers, etc. In the aggregate these miscellaneous services consume enormous numbers of cells, but they are so numerous, and there are such variable conditions prevailing in each kind of service, that it would be useless to attempt to develop standard tests covering them.

It is not difficult for anyone particularly interested in any special service to arrange a suitable test for himself. Care should be taken to make the conditions of test, viz., number of cells, resistance in circuit, period of drain, etc. approximate those of the service in question.

RATE OF DETERIORATION ON OPEN CIRCUIT.

The voltage and short circuit current of the cells for test are read initially in order to insure that the cells are in good condition. The cells are then stored in a dry place of normal room temperature.

The following readings are taken:

1. Initial voltage and short-circuit current.

2. Short-circuit current at the end of four weeks, eight weeks and each eight weeks thereafter.

3. Voltage at the end of six months.

The cells are kept on the shelf until the short-circuit current has fallen below 10 amperes. This point is arbitrarily chosen, as it represents a point below which it would be difficult to market the cell. For practical purposes, the results are expressed as the number of months during which the short-circuit current remains above this cut-off point. Much more meaning, however, is attached to the rate at which the current falls, generally reported as the drop in amperage for a given period expressed as a percentage of the initial amperage. This is especially true when investigation of the quality of cells is the object. For practical purposes, however, the first rating given, i. e., months to 10 amperes, is perhaps preferable.

Notes: The results from this test are largely indicative of increase in internal resistance, and bear no definite relation to the service which the cells may give. However, this information, coupled with familiarity with a brand of cells, becomes a very good indication of its quality. It also serves to indicate any serious defects of manufacture.

The ammeter for reading short-circuit current should be dead-beat, and with its leads should have a resistance of 0.01 ohm. Two 30-inch lengths of No. 12 lamp cord make very convenient leads.

Particular attention should be given to the temperature at which cells are stored, as the rate of deterioration is influenced to a marked degree by the temperature of the cells.[9]

The ideal method for an open-circuit deterioration test would be the determination of the decrease of service capacity due to

[9] Trans. Amer. Electrochem. Soc., **17**, 357 (1910); **19**, 39 (1911).

storage over definite periods. This practice, however, would entail much labor and expense where the amount of testing to be done is large.

THE ADAPTABILITY OF TESTS TO THE NEEDS OF THE VARIOUS CLASSES OF CONSUMERS.

The question may arise in the mind of the consumer as to what extent the cells he purchases should be tested. It obviously would not be practical for the small consumer to conduct tests on the same scale as those carried on by a consumer using many barrels of cells per year. It is impossible to formulate any set rules for sampling and testing for any consumer or group of consumers, as the amount of testing done must be regulated by the relation of the cost of testing to the value of the cells purchased. However, we present here suggestions as to the adaptability of these methods to several roughly classified groups of consumers.

The Small User:—In this class may be included the great percentage of consumers. The man who buys a few cells at a time for purposes of ignition, bell ringing, etc. Obviously it is out of the question for this class of consumers to conduct any sort of service test. The only safe course is the purchase of a reputable brand of cell. We would advise that, perhaps, every cell purchased thereafter be read for short circuit current, although as stated previously, this reading gives no direct indication of the service capacity of the cell, yet, if the reading is normal for that brand, it may be reasonably certain that the cell is in good condition and that it will probably give as much service as those of the same brand formerly purchased.

It would be impractical for the small user to provide himself with an expensive ammeter, as, for his purpose, a good make of pocket instrument will give readings sufficiently accurate. Such instruments, however, should be checked up occasionally with a standard meter.

The Small Dealer:—This class comprises those dealers who may dispose of from a few hundred to a thousand or more cells per year. The dealer is particularly interested in keeping the quality of his stock up to the standard. As cells are received

a representative sample, *e. g.*, 10 percent chosen at random throughout the lot, should be read with a reliable make of ammeter. If the readings are normal it would scarcely profit to make any further tests. For his protection all cells should be read with the ammeter before being delivered to customers.

The Jobber:—The jobber buys and sells dry cells largely by barrel lots, and in many cases conducts no tests whatever. If he is desirous of keeping his quality strictly up to standard it would be well to open several barrels in each shipment and test with an ammeter a dozen cells chosen at random throughout the barrel.

If the large jobber wishes to carry the best grade of cell for any service, it would probably pay him to conduct the recommended telephone and ignition tests on a small scale. The consumer however has more interest in the service to be obtained from cells than has the jobber, but as noted above the small average number purchased by the consumer prohibits tests of any magnitude. Therefore if the jobber takes up dry cell testing seriously it would be with the ultimate aim of protecting, and building up the reputation of the small consumer.

Telephone Companies:—

1. The small telephone company consuming say less than ten barrels of cells per year could install a standard telephone test of small capacity by fitting suitable electrical contacts on a clock and connecting these with a telegraph relay in such a way as to cause the latter to open and close the dry cell circuits. We would advise that such a test be maintained by each company and that periodical tests (at least four per year) be made on the shipments of cells received and also on small lots of other brands purchased from time to time for the purpose of test. The small company should also test a representative sample (say 10 percent) of all consignments received, with a good ammeter.

2. The large telephone company using many barrels of cells per year can well afford to install an apparatus for carying on the test suggested in this report. We would advise that a battery of three cells from each consignment received be placed upon the telephone test. We would however, consider two such tests

per month as a safe maximum number of tests. In addition the short-circuit current and open-circuit voltage should be read upon a representative sample of all cells received.

It would be profitable for the large telephone company to conduct regular telephone tests, not only upon the batteries used with their equipment, but also batteries composed of the different makes of cells, in order to compare their relative merits on telephone service.

Gas Engine Manufacturer:—To the gas engine manufacturer it is important that the batteries furnished with his engine be the best cells obtainable from an ignition standpoint. As the apparatus necessary for carrying on the ignition test is quite inexpensive and as the test requires very little attention, the manufacturer of such engines purchasing a considerable number of cells should conduct the ignition test not only as a check upon the cells he is receiving, but as a basis for judging the merits of the different grades of ignition cells on the market.

An ignition test upon six cells from every fifth barrel received with a maximum of two tests for a single consignment of cells, would probably be sufficient. Before being sent out with an engine the short-circuit current on all cells should be read and those reading abnormally low (*e. g.*, 5 amperes or more below the average for the brand and grade) should be rejected.

C. F. BURGESS, *Chairman,*
J. W. BROWN,
F. H. LOVERIDGE,
C. H. SHARP,
Committee on Dry Cell Tests.

DISCUSSION.

PROF. C. F. BURGESS presented the paper, and in doing so said: This report is devoted to a consideration of methods of testing a piece of electrical apparatus to which very little attention has been paid, although a type of apparatus of great importance.

The members of the Society and the members of the committee have been familiar with the dry battery test largely from the

standpoint of the manufacturer, but in formulating this report we have attempted to look at the matter from the standpoint first, of the small user, and then, from the standpoint of the larger user, and finally, from the standpoint of the manufacturer.

We hope the report will bring out a free discussion, not only orally, but communicated, and we will not feel at all displeased if this discussion is of an adverse nature. Any one who looks at this matter of dry battery testing will see that it is a complicated problem, there are so many different factors entering into it that it is difficult to devise perfectly satisfactory methods of testing, and we will welcome criticism of our report.

This report is presented, not with the idea that it will be accepted as a final report on the question at this time, but with the hope that it will, at least, be put into print under the auspices of this Society, and that it will go into the hands, in some way or other, of the battery users, that there will be attention paid to the matter of testing dry batteries during the coming year, and that we will have a record of tests presented giving the results of dry battery performance. This is, then, a tentative report, with the hope that at some future day this committee, or some other committee, will present a final report, which will be accepted by the Society.

MR. F. H. LOVERIDGE (*Communicated*): With reference to the E. M. F. test to "*determine the condition of cell before use,*" the writer is of the opinion that no reliance can be placed upon such test made with a high resistance voltmeter. The resistance of the instrument is so high compared to the cell itself that a cell which has seen considerable service might not give any indication of its condition.

Furthermore, cells that have shown excellent results in service and on shelf have shown voltage readings that varied in amount from less than 1.45 to over 1.60, thus indicating that the E. M. F. of cells is no safe criterion of what may be expected in service.

It should be added that these observed voltages were readings from cells that had not been sent out from the factory, and also that readings were taken after the regular time for the cells to settle down to normal had elapsed.

It is generally recognized that the effect of service on a dry

cell is an increase in its apparent internal resistance rather than the loss of E. M. F.; it is not at all uncommon to find cells that will give a high voltage reading on a high-resistance voltmeter, but which are capable of giving only a very feeble short-circuit current. It then seems logical to assume that E. M. F. readings are of no particular value taken by themselves, but must be accompanied by some data as to current flowing. This naturally leads to the idea of ignoring E. M. F. and depending on current readings with a suitable resistance in circuit to represent the class of service for which the cell is to be used. The factor of length of time on closed circuit would also be dependent on the class of service. This plan is applicable to life-tests, and would have the advantage of somewhat simplifying them. It would have its best application, however, in the testing of cells in service, to ascertain their condition at any particular time.

For such a test an ammeter, having, in series, a resistance equaling that of the circuit in which the cell is used, would be the best arrangement. The ordinary pocket instrument would not be found satisfactory for this test, for the reason that the deflection of the ordinary instrument will remain at a fixed point and not show a change as the current diminishes. The only satisfactory instrument would be one in which changes of current would produce corresponding changes in deflections. A test of this nature would also be much more consistent for cells that had deteriorated to a certain extent in storage, than the test made with a low-resistance ammeter for instantaneous short-circuit current.

The internal condition of a dry cell in service is known to be dependent on a number of influences, but I believe it will be conceded that the factors of greatest importance are amount of current flow, ratio between open- and closed-circuit periods, and the arrangement or distribution of these periods over the day.

It being granted that this is the case, it follows that the more nearly we can approach actual service conditions the more nearly we will have accurate information as to results that may be expected, although it does not necessarily follow that accuracy of results is strictly proportional to the approach to actual conditions of service. This is true whether tests are made for purposes of ascertaining what may be expected from a particular

make, or for comparison between various makes (each possessing more or less individuality), to determine which is best adapted for a particular purpose.

For the above reason, I would be strongly in favor of recommending that wherever practical, all battery life tests either duplicate the conditions of average service or else that readings from cells in actual service be taken, if conditions are such that there is a uniformity of service requirements for all cells.

This last condition is seldom met with except where cells are employed with some uniformly operating mechanism, but, even in this case of uniform conditions of circuit closure, other factors, such as temperature, are liable to enter.

Following the above recommendation, it would be desirable to describe specific tests to meet the requirements of the different general classes of service.

MR. W. B. PRITZ: It is true that the internal resistance of cells increases during service, and that the voltage, decreased by polarization, will recuperate greatly when the circuit is broken. End points in service tests cannot therefore be determined by open-circuit voltage readings.

The voltage measurements referred to in the report, however, are those taken while the circuit is closed, *i. e.*, while the cell is discharging. As these readings measure that part of the total E. M. F. of the cell used in forcing the current through the external circuit, such readings give precisely the same information as would be obtained from the readings suggested by Mr. Loveridge, *viz.*, readings of the current flow in the circuit. However, in the ignition test recommended in the report, the end point is determined by a current impulse value, for reasons fully stated in papers which have been presented before this Society and referred to in the report.

Relative to Mr. Loveridge's suggestion that the conditions of test be made to conform as closely as possible to the conditions of service, it may be said that this is in some cases most desirable. However, as brought out in the report, when simply a comparison between cells is wanted, a close approach to service conditions is fully satisfactory. Tests which will conform strictly to actual service conditions, could they be devised, would, in most cases,

be very complicated and would require a great deal of expensive apparatus and for most purposes would be unnecessary, since simpler tests will serve to classify the different brands of cells according to their service capacities.

Conditions surrounding service in which dry cells are used, in the main, vary from time to time and also between different installations, so that in the majority of cases it is impossible as well as unnecessary to duplicate such conditions in a test. As close an approach as possible to operating conditions, at the same time retaining simplicity, is to be desired.

MR. J. FRANKLIN STEVENS (*Communicated*): In the "Report of Progress by the Committee on Dry Cell Tests," Section 2, page 279, after reciting several excellent reasons why the short-circuit current test is meaningless, without mentioning, however, the damage done the cell by short-circuiting it, full directions for making such tests are given. The directions state: "The ammeter for reading short-circuit current should be dead-beat * * *. The maximum swing of the needle should be taken as the short-circuit current of the cell." Further on it is stated: "For accurate measurement of the short-circuit current of a new cell, cheap instruments of the pocket type should be avoided."

Without attempting to discuss the advisability of the short-circuit current test, which is both harmful to the cell and meaningless as to results, I would call attention to the fact that, if the Committee decides to retain this test, the reading obained by noting the maximum swing of the needle gives no quantitative measurement of the current and a qualitative measurement only when the same ammeter is used on cells of the same capacity, that is cells giving approximately the same short-circuit current.

Indicating or direct-reading ammeters are not designed for use as ballistic galvanometers, in fact they are designed to be as aperiodic or dead-beat as possible, but in this respect no two are alike. Even ammeters of the same make and of the same range will differ sufficiently in their aperiodic qualities to prevent the overthrow of the needle giving an accurate relative measure of the current. This difference will be far greater when results are compared between ammeters of different makes and different ranges, at various parts of the scales.

The Bureau of Standards recently completed a series of tests on eight makes of American direct-current voltmeters and ammeters (see Bulletin of the Bureau of Standards, 7, No. 3), in which they determined, among other things, the damping or dead-beat qualities. Testing voltmeters of 150 volts maximum range on a circuit of 120 volts, the time required for the pointer or needle to come to rest after closing circuit varied from 0.8 to 4.8 seconds. In the ammeter tests, employing a current of 160 amperes on instruments of 200 amperes maximum range, the time required for the pointer or needle to come to rest after closing circuit varied from 1.1 to 5.8 seconds.

The damping or dead-beat qualities of any direct-reading instrument depends upon a number of factors entering into the design and construction, such as torque, weight of moving element, friction, strength of field, and moment of inertia of the moving element, while the overthrow or maximum swing of the needle depends not only on these factors but also upon the momentum given the needle when the circuit is closed. This momentum is also directly proportional to the ratio of the current through the instrument to the total maximum current capacity of the instrument, that is, for example, the actual amount of overthrow of the needle will be greater at 2/3 of full scale than at 1/3.

Since the overthrow reading is in no sense quantitative, it is a matter of indifference whether the ammeter employed for such a test is a high-grade accurate and aperiodic instrument or a cheap type of pocket ammeter.

A consideration of the facts above makes it apparent that a measurement of short-circuit, or any other, current based upon the "maximum swing of the needle" is entirely valueless as a measure of the current or even as a basis of comparison between cells of different capacities.

Dr. John W. Brown: The discussion, as I take it, deals with fractions of a second, that is the taking of readings in a small limit of time. The present way of measuring the short-circuit current of a dry cell usually requires a contact of one or two, or perhaps three seconds, and in that time it gets down

to a perfectly definite reading. We are not interested in general in readings taken as indicated in that discussion.

PRESIDENT WHITNEY: It seems to me that the Society should only support a report which is practical. If we get out a report which covers a method of testing dry cells which the users will not recognize, then there is little use in our getting it out. The object of our Committee has been to study the different uses of the dry-cell battery in the various fields, to secure the best method whereby the test can be made, and to recommend a form of test which will be practicable and will be used.

It was my hope that the discussion this morning, by men who know more about it than I do, would lead to suggestions of methods for making the test in a practical manner.

PROF. JOS. W. RICHARDS: I move that this report be received and the Committee continued, to report at a subsequent meeting.

DR. CARL HERING: I second the motion.

(The motion was put to vote and carried.)

PRESIDENT WHITNEY: I think that this is a good move. Many people who are using dry batteries may be led to test them under the conditions presented in the report of the Committee, and report their conclusions to the Society.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

PERFORMANCE OF DRY CELLS.

By Carl Hambuechen.

Since 1908 the writer has made examination and tests on several thousand dry cells for the purpose of determining their characteristics and performance as judged by methods of testing in common use. The cells examined included the products of various leading manufacturers supplying the American market. This work has done for the French Battery & Carbon Company, of Madison, Wisconsin, and it was through the courtesy of this company that permission was secured to draw upon the records for information which may be of some general interest to dry-cell users.

There are three important characteristics of dry cells by which merit is judged, these being commonly designated as the "flash" or "short-circuit current," the "shelf life" and the watt-hour output or "service capacity."

The first is of the least importance and the last is the most important, as determining the actual merits of the product, but as to the frequency of use this order is reversed, and it is by the flash test that the largest proportion of dry cells sold are judged. The dealer tests the barrel of dry cells when received by means of the ammeter, the customer in turn goes over the dealer's stock and picks out cells which show the "most amperes." To those who have given the matter some thought it is evident that the merits of the cell cannot be determined solely by the initial amperage, but the test is nevertheless in general use and is an important factor. The principal reason for this test is apparently its simplicity and rapidity, coupled with the fact that it does tell whether the cell has a high or low internal resistance and whether it is alive or dead. This test being used as an indication, it is natural that the purchaser would choose cells which show the highest test, that the dealer therefore finds it easier to sell a

higher testing product, and that this influence extends to the maker in prompting him to turn out a high-testing product.

That there has been a tendency in this direction during the past few years, of increasing the flash test, is indicated by the curves in Fig. 1. These were compiled from many observations of the standard size 6 inches (15 cm.) high by 2½ inches (6 cm.) diameter dry cells of the most prominent makes.

Thirteen years ago comparative tests were made on twelve different brands of dry cells on the American market; these tests being carried out in the Applied Electrochemistry Laboratory, of the University of Wisconsin. They indicated that the flash test or initial amperage of cells at that time varied between two and

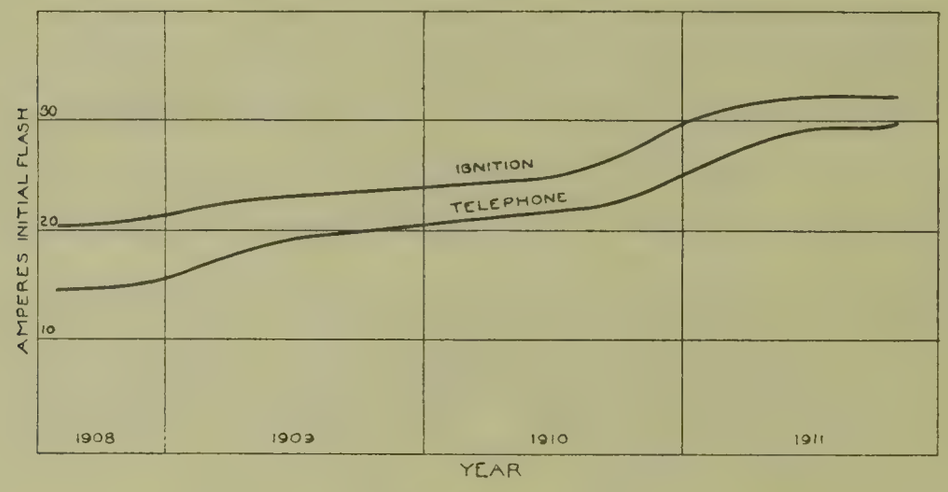

FIG. 1.

ten amperes. There has been a gradual upward tendency since that time, and that this upper tendency is still continuing is shown by the curves above referred to. An attempt has been made to separate the 6 in. (15 cm.) dry cells into two classes, namely, those intended for telephpone service, door bell and signal work and the like, and those intended for gas-engine ignition. It will be seen that since 1908 the initial amperage of the ignition type has been raised from 20 to over 30 amperes, while with the telephone type the amperage has been raised from 15 to nearly 30 amperes. In considering this decided upward tendency it is interesting to speculate how much further it will be carried, and as to whether the other and more important characteristics of dry cells are being likewise improved.

There are various methods by which the initial amperage may

be increased, including the use of graphite and higher conductive carbon, the increase in the percentage of this material with a corresponding decrease in the manganese and other constituents, by the use of various chemicals which increase the activity, by the use of thinner and more porous lining for the cells and by the density and hardness of tamp, etc.

The question naturally presents itself as to whether in the attainment of a high flash some of the other desirable characteristics may not be sacrificed, and from the writer's observation it appears that during the past three years there has been little if any improvement in the cell durability or shelf-wear or in the watt-hour capacity; in fact there is some evidence that these important qualities have been sacrificed in the attainment of high amperage.

There is an impression which is becoming more generally recognized that high amperage alone is a false criterion, and that a cell possessing it is likely to suffer more rapid deterioration either in storage or for long time service. In all probability the adoption of certain simple and standard methods of testing will result in more attention being given to the more important characteristics of long life and energy output.

While there are certain classes of service in which the dry cell is naturally expected to run down within a few weeks, there are larger fields for usefulness where the service must be extended over many months and even a year, and in which deterioration when the cell is not in use naturally plays a prominent part. These classes of service include telephone, signal and alarm service, and where the dry cells are used as an emergency reserve in the failure of other sources of electrical energy supplied.

A question of great importance and upon which there is little published information is this, "What is the rate of normal shelf-deterioration for a standard well made cell under normal temperature conditions?" From statement by Mr. D. L. Ordway, Transactions of the American Electrochemical Society, **17**, page 349 (1910), the shelf life of a cell may be taken as the number of months before the short-circuit current reaches 10 amperes. This 10 amperes is taken not because it indicates a corresponding decrease in the output capacity of the cell, but because it repre-

sents a value such that the dealer could not dispose of the cell to the average consumer. The best cells in the market have a shelf life on this basis of 12 to 15 months, while 10 to 12 months is given as more nearly the shelf life obtained with the high-grade cells now on the market. Mr. W. B. Pritz, Transactions of American Electrochemical Society, **19**, 39 (1911), gives data showing the variation of shelf deterioration at various temperatures. At 25° C. at 22-ampere cell will drop 10 percent in amperage in ten weeks on open circuit.

From a large amount of data the writer has endeavored to compile a curve which will show a normal deterioration of the more prominent types of cells on the market during the past

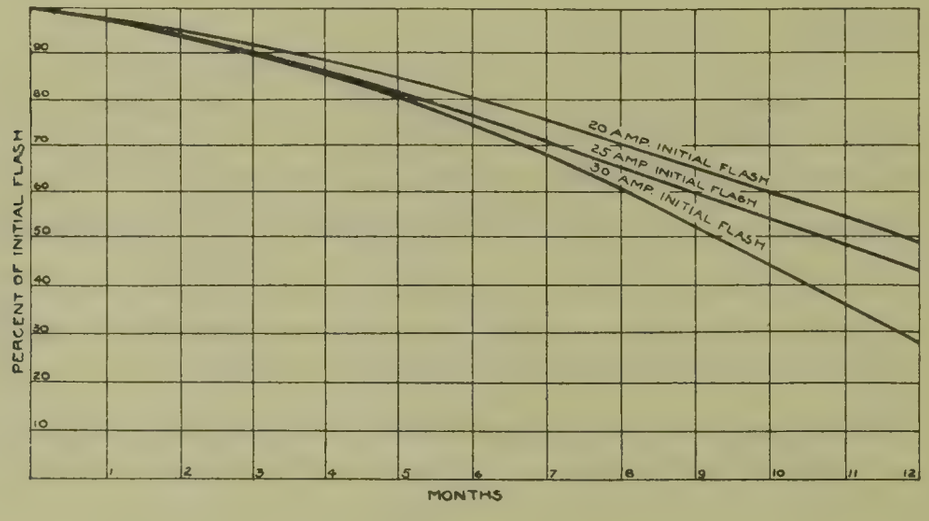

FIG. 2.

year. This is difficult on account of the wide variation in performance, not only as among cells of different makes, but even as among cells of any one make. Basing judgment upon the results obtained from over a thousand cells made in the latter part of 1910 and during 1911, the curves in Fig. 2 may be taken as representative of the better grades of 6 in. (15 cm.) dry cells. These curves express the percentage of the original flash which cells should show after various intervals of storage up to one year. It has been observed that cells made with higher initial amperage show a more rapid deterioration than those made initially of the lower flash test as indicated by the three curves for cells having initially 20, 25 and 30 amperes respectively. It has been pointed out by Messrs. Pritz and Ordway that the falling off in flash tests does not by any means indicate a corresponding

reduction in useful service capacity, and the writer wishes to confirm these observations. Nevertheless, it is desirable that cells be improved for shelf wear and the above curves indicate that marked opportunity for improvement exists.

It is hoped that more attention may be given during the coming year to dry-cell testing, especially along such standard lines as may be recommended by the American Electrochemical Society, and that later results may be presented by various observers through which more accurate knowledge concerning dry cells may be derived.

Northern Chemical Engineering Laboratories,
Madison, Wis.

DISCUSSION.

PRESIDENT WHITNEY: It seems to me that we might get a flash test which would partly ruin the cell, and our Committee should do what it can to get a proper kind of test. The "flash test" is such an easy thing that there is a possibility of its being abused.

PROF. C. F. BURGESS: The flash test is used on millions of cells and by many users throughout the country. It shows them something about the apparatus, at least whether the battery is alive or dead. The battery manufacturers use a flash test on the cell to show something as to its characteristics. Most people who buy a 15-cent or 25-cent dry-cell cannot afford to have a $10 instrument to test it with, so that we are forced to face the necessity of $1.50 pocket instruments, and it is in some respects rather out of the question to say they cannot be used, because they are used and will be used. The best thing we can do is to find out what such readings mean, and thus help the situation to a certain extent.

DR. J. W. BROWN: Some companies, the National Carbon Co. included, have tried for a long time by means of an educational campaign to convince the people of the limited amount of

information which is derived from the "flash test," but, nevertheless, the flash test is made and we are obliged to accept that fact. Accepting that fact, we want to point out the dangers of too broad a conclusion from a test of that sort. In talking with a great many persons personally, I have found some difficulty in persuading them that if a cell shows at the outset 25 amperes, and on a later test shows 12.5 amperes, or thereabouts, that less than half the energy has disappeared from the cell. It seems self-evident to most people that a 50 percent loss of energy has occurred. This point was brought out and emphasized at considerable length in the report of the Committee, and, confirmed by the Society, should have considerable influence with the users of dry cells.

President Whitney: In practice, any test short of a life test is not a good test. It is not true that a man must make the test on every new battery. It seems to me that the test should be made by an organization like the Bureau of Standards, and random samples taken from large consignments for test.

Dr. Carl Hering: Exactly; and a parallel case is the testing of incandescent lamps.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE REGENERATION OF SULPHATED STORAGE CELLS.

By C. W. Bennett and D. S. Cole.

In a recent article by Mr. G. A. Perley,[1] a method for curing sulphated storage cells was outlined. The work consisted essentially in experiments on the reduction of lead sulphate by three methods, namely, chemical reduction, electrolytic deposition and reduction, and chemical solution followed by reduction.

By the first method ferrous sulphate and sodium hydroxide, zinc and hydrochloric acid, zinc precipitated electrolytically on the plates, and aluminum with potassium hydroxide, were used as reducing agents. The third reducing agent gave a partial reduction of the sulphate, but it was found that in order to get enough zinc on the plate the current density had to be increased. However, with the increased current density the zinc precipitated on the best conducting portions of the grid and the lead sulphate, which of course formed the non-conducting part, was found to scale off, due to the increased potential difference required to force the higher current through the solution. Straight reduction, therefore, of the lead sulphate was given up.

Since in the normal working of a cell lead is left in intimate contact with lead sulphate, which is readily reduced on account of a local couple, probably, it seemed best to try precipitating lead on the lead sulphate and then charge the grid in sulphuric acid. This would give, apparently, normal working conditions. In order to do this, lead was precipitated from lead plumbite, lead fluosilicate, lead acetate, and lead perchlorate solution. The difficulty found here was, that by "treeing" the lead flaked off and caused a large amount of shedding and hence loss of the active mass. For this reason this method was considered unsatisfactory.

[1] Jour. Phys. Chem. **15**, 489 (1911).

It was found, rather by accident than otherwise, that a sulphated grid when placed in sodium hydroxide solution became reduced to lead very quickly. In order, therefore, to obtain a sodium hydroxide solution in the pores of the lead plate, where the largest tendency to sulphate is found, electrolysis with sodium sulphate as electrolyte suggested itself at once. The current should be sent through the cell in the direction of charging; sodium hydroxide will be formed at the lead plate, and sulphuric acid at the lead dioxide plate. Thus an alkaline solution will be formed at the cathode and an acid one at the anode.

Now, if the electrode potential for the liberation of hydrogen be measured, a higher voltage is found necessary when an alkaline solution is used than that required for a neutral or acid solution. In the same way a higher voltage is required for the liberation of oxygen in acid solutions. The discharge potentials for hydrogen and oxygen, respectively, will therefore be increased over those in a straight acid solution. In this way the range of reduction and oxidation will be increased, for a higher voltage can be impressed without the liberation of hydrogen and oxygen. Thus there is a greater tendency to reduce lead sulphate to lead at the lead plate or cathode, and oxidize lead sulphate to lead dioxide at the lead dioxide plate or anode.

When this was tried on cells that were uniformly coated with lead sulphate the results were astonishing. Cells with a capacity of one ampere minute were brought back to their original rated capacity, and in some cases to a capacity over 100 percent of the original rating.

The concentration of sodium sulphate recommended, which can be varied within wide limits, is 200 grams of the crystallized salt ($Na_2SO_4.10H_2O$) per liter. The sodium sulphate should fulfill, as regards purity, the requirement for battery acid, that is, it should be chemically pure. It is not necessary to wash out all of the sodium sulphate; the plates need only be dipped once in water. The time of charging in the sodium sulphate solution, for the worst cells, was about 60 hours, at the 8-hour rate.

In order to verify these results on a larger scale than had previously been tried, it was thought desirable to treat a battery belonging to the Department of Electrical Engineering, of Sibley

College, Cornell University. The battery consisted of 52 cells, and had been in use for five or more years with very little attention. The cells were used daily by students in the laboratory, throughout the school year, and had been put out of commission for the summer months in the usual way, by removing the plates from the acid, allowing them to stand for 24 hours in water, and then drying. In the spring of 1911 the cells were not allowed to stand long enough in water and hence were very badly sulphated in the fall. They were put back into commission in the usual way, and were found to have very much less than their rated capacity of 60 ampere hours.

During the Christmas holidays just passed the cells were treated by the method above outlined. A capacity and efficiency run was made on the battery before treatment. The power was measured by a watt-hour meter. The current was kept constant at the 8-hour rate, namely, 7½ amperes. The results of this first run are given in Table I below:

TABLE I.

Efficiency and Capacity Test Before Treatment.

Total input	7,150 watt hours
Total output	3,040 watt hours
Ampere hour output	30.6 ampere hours
Energy efficiency	42.5 percent
Energy capacity, of rated*	48.7 percent
Ampere hour capacity, of rated	51.0 percent

From this it can be seen that the active mass of the cells was about half converted into sulphate in the non-available form when used in the ordinary battery acid.

After this the acid was removed, the plates dipped in water, and the jars filled with a solution of chemically pure sodium sulphate. The anhydrous salt was used and the solution contained 10 percent of this salt, by weight. This corresponds to 22½ percent of the crystallized salt if this be used. The battery was then charged in the usual way at the 8-hour rate for 53 hours.

A motor generator was used to supply the power necessary. The generator was driven by a three-phase induction motor. The power being available only from 6 A. M. to 12 P. M., an

*This rated capacity was calculated, allowing two volts and sixty ampere hours per cell.

automatic device was employed for starting and stopping the experiment by opening and closing the generator circuit. The induction motor was left across the line at night. As it is customary to build up the voltage from 0 to 2,200 volts at the power-house without disconnecting the transformers from the line, the motor started easily without giving any trouble. In the morning the battery circuit had to be closed when the generator was delivering about three-fourths of the voltage required for normal running, for owing to the diffusion of the electrolyte the back electromotive force of the battery had dropped during the night. A solenoid was therefore designed to close the generator circuit at about three-fourths full load voltage on motor. At this instant the motor was running at about three-fourths full load speed, and the generator was thus delivering about three-quarters normal charging voltage. This would then start the charge at a lower rate and gradually increase the current as the polarization of the cells increased. At night when the power was turned off the solenoid was no longer energized, and the plunger dropped out, thus opening the battery circuit.

After the charge was completed, which can be judged by the total reduction of the sulphate on the inner sides of the plates, the plates were removed, dipped once in water, and replaced in battery acid of specific gravity 1.23. In order to get a capacity and efficiency test the battery was then discharged, charged, and discharged a second time. The results after this treatment are shown in Table II.

TABLE II.

Efficiency and Capacity Test After Treatment.

First discharge, output	6,250 watt hours
First charge, input	6,820 watt hours
Second discharge, output	5,530 watt hours
Ampere hour output	58.1 ampere hours
Energy efficiency	81.1 percent
Energy capacity, of rated	88.7 percent
Ampere hour capacity, of rated	96.9 percent

The efficiency and capacity tests were made on second discharge, it being evident from the above figures that the first discharge shows the cell in an overcharged condition.

From a comparison of Tables I and II it is seen that the energy efficiency has been increased from 42.5 percent to 81.1 percent. The energy capacity of the battery has been increased from 48.7 to 88.7 percent. The ampere hour capacity has been increased from 51.0 percent to 96.9 percent of the rated.

The battery was out of commission, for treatment, three days. This does not count the time required to take the efficiency runs as herein given.

The cost of regenerating the battery included the following items:

68 pounds anhydrous sodium sulphate, C. P.	$4.80
10 hours unskilled labor, at 20c.	2.00
5 hours at 30c.	1.50
50 kilowatt hours power at 5c. per K. W. H. (by watt hour meter)	2.50
Total	$10.80
Total cost per cell	$0.208

Reducing this to a commercial basis it may seem advisable to charge the loss of the use of power from the battery, while out of commission. The rated capacity of the battery is 6.24 kilowatt hours. At 48.7 percent capacity before treatment, the capacity was, therefore, 3.04 kilowatt hours. The battery was out of commission for 54 hours, which would allow three discharges. Therefore the total power loss was $3 \times 3.04 = 9.1$ kilowatt hours. Estimated at 5 cents per kilowatt hour, this represents a loss of 46 cents. This would raise the total cost of the regeneration to $11.26, or an increase of nine-tenths of a cent per cell.

The increase in efficiency represents a gain in output of 2.5 kilowatt hours per discharge at the normal rate of charge. At 5 cents per kilowatt hour this totals 12½ cents. The total cost of the experiment was $11.26. Dividing this by 12½ cents gives 90. This means in 90 charges and discharges the saving of power, due to the increased efficiency, would pay for the regeneration of the cells.

The storage battery concerns claim that the same results can be obtained by prolonged charging at half the normal rate. This is no doubt true for cells that are not badly sulphated. While no direct measurements have been made along these lines,

indications from observations in this laboratory point to the fact that a battery would have to be out of commission from three to four times as long as that required by the above outlined sulphate method. It has also been noticed that prolonged charging causes excessive shedding of the active mass and hence its total loss.

Conclusions.

The conclusions drawn from this experiment may be summed up as follows:

1. Badly sulphated cells can be economically regenerated by electrolysis in sodium sulphate solution.

2. The cost need not be greater than 20 cents per cell.

3. Allowing 5 cents per kilowatt hour for power, the increase in the efficiency of the cell will pay for the regeneration in about 90 charges and discharges, or in about 3 months' daily use.

Cornell University, Ithaca, N. Y.,
January, 1912.

DISCUSSION.

DR. W. LASH MILLER: A good many of us will try this experiment this winter and present the results at the next meeting.

DR. W. D. BANCROFT: All good things have a bad side. This method, I think, will regenerate any cell which has gone to pieces owing to sulphate. On the other hand, we have been running some tests this year on automobile batteries which have dropped down to 50 percent of their rated capacity. You cannot improve these; the trouble is that they have not sulphated, they have suffered from shedding.

MR. F. P. H. KNIGHT (*Communicated*): I have used sodium sulphate in several "6—60" ignition batteries with excellent results. I used about 10 grams of C. P. sodium bicarbonate to each cell, containing about 500 or 600 c.c. of electrolyte.

One battery was in such bad shape that it took 15 volts to

force 1 ampere through it, but two or three minutes after the sodium sulphate was added, voltage and current became normal.

I made no attempt to remove the sodium sulphate, even partially, and so far (six months) I have noticed no bad results. It is interesting to speculate as to whether any such will show up later.

DR. BANCROFT: In many cases people have added caustic soda, more often sodium carbonate, to their storage battery cells, and, according to all accounts, have gotten very beneficial effects therefrom; the next man will do the same thing, under similar circumstances, and will say that he did not get any beneficial effects. The great trouble there is they have only added a small amount—what you have then is sodium sulphate, plus sulphuric acid, and what you need to get the best effect is to have a sodium sulphate solution, and not a sodium sulphate solution containing a large amount of sulphuric acid. That is why the earlier work which was done did not turn out anything like as satisfactorily as was anticipated. There are plenty of references in the scientific literature from which you can make your choice as to whether it is a good thing or not. We do not advocate the addition of a small amount of sodium carbonate to the electrolyte. We say that you should take out the electrolyte, and put in a sodium sulphate solution, afterwards replacing the electrolyte.

DR. CARL HERING: Unless I am very much mistaken, we used to regenerate badly sulphated negative plates of accumulators by connecting them with a piece of zinc, immersing them in sodium sulphate and letting them stand; they are reduced by their own current.

MR. CLAYTON L. JENKS (U. S. Patent Office, Washington) (*Communicated*): I beg to enclose three U. S. Patents which may be of interest in furthering the discussion of Messrs. Bennett and Cole's paper.

[Abstracts by the Secretary]: U. S. Patent 867,517, of October 1, 1907, to Henry Leitner, concerns *preparing* electrodes for secondary batteries by using them as anodes in a weak alkali sulphate solution. U. S. Patent 915,980, of March 23, 1909, to Carl Luckow, concerns *regenerating* accumulator electrodes by using them as electrodes in a greatly diluted alkali sulphate solution, the

usual acid being drained out of the cells and the 1 to 2 percent sulphate solution substituted. U. S. Patent 990,661, of April 25, 1911, also to Carl Luckow, concerns *regenerating* accumulator electrodes by a modification of the preceding method.

Mr. C. W. Bennett (*Communicated*): As to the formula used by Mr. Knight, the concentration of sodium sulphate is from 1.5 to 2 percent of the salt placed in the regular acid. There is nothing novel about this use of dilute sodium sulphate in the storage battery. This has been known for years, and, in fact, has been practiced with experimental cells in the laboratory at Cornell. This action of sodium sulphate was published by Gladstone and Hibbert,[1] and the concentration recommended was:

Sodium sulphate, anhydrous	0.81	percent
Sulphuric acid	29.39	"
Water	69.80	"

In regard to the patent[2] suggested by Mr. Jenks, it is only necessary to say that this patent covers a method of forming Planté plates, and has nothing to do with the treatment of sulphated cells. It is interesting to note that this process of using high current densities and cooling the solution was practically the scheme followed by the Westinghouse Battery Company before it ceased operations.

The second patent[3] by Luckow is quite a different process from the one outlined in this paper. A dilute solution is used, with a current density of from 0.01 to 0.03 ampere per square inch. The charge is given in the reverse direction for from 4 to 8 days, after which the current is again reversed for from 3 to 6 days. The cell has, therefore, been carried through a reversal, and the time required is from 7 to 14 days.

In the last patent[4] the method is changed slightly, so that very dilute acid is substituted for the sodium sulphate solution. The reduction of the lead sulphate is carried out in this solution by charging in the reverse direction. After this, a solution of sodium sulphate is used for reversing the cell. It must be remembered

[1] Philosophical Magazine, **30**, 162 (1890).
[2] U. S. Patent 867,517, October, 1907.
[3] U. S. Patent 915,980, March, 1909.
[4] U. S. Patent 990,661, April, 1911.

that the sodium sulphate, according to the claims of the patent, can have nothing to do with the reduction of the lead sulphate, but is used as a convenient solution in which to reverse the cell. The reason for the use of such a solution will be readily apparent to those who have carried out the rather delicate operation of reversing a cell by charging in the regular battery acid. This method requires from 8 to 15 days, since a very low current density, as before, must be used. This method will give satisfactory results with cells which are not too badly sulphated. If the cell be completely sulphated, however, it cannot be reduced in acid solution,[5] as has been repeatedly shown, and referred to in the first published account of this method,[6] outlined above.

The method outlined above regenerates any cell, no matter how badly sulphated, in not more than 60 hours time for the worst cell. In other words, lead sulphate may be reduced in this solution. The current density used is about 0.05 ampere per square inch of positive plate surface, or, in other words, the normal rate of charge. No reversal is necessary, the current being sent in the direction of the charge from the start. A saturated solution can be used, if desired.

[5] Gladstone and Hibbert, *l. c.*, p. 165.
[6] Jour. Phys. Chem. **15**, 489 (1911).

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE EFFECT OF ADDITION SUBSTANCES IN LEAD PLATING BATHS.*

By Frank C. Mathers and O. Ralph Overman.

Historical.

The addition of small quantities of certain substances to electroplating baths increases the density, brightness and non-crystalline character of the deposited metal. The use of these so-called addition substances has been practised for many years. In 1847, Milward[1] discovered that the addition of small amounts of carbon bisulphide to silver plating baths caused the deposit to show greater lustre and brilliancy instead of the dead appearance when no addition substance was used. Solutions of iodine or gutta-percha in chloroform, or some heavy hydrocarbons, oils, tars,[2] etc., also improve the silver deposit.

In the deposition of iron upon moulds for reproducing engraved surfaces, a small addition of gelatine improves the deposit.[3]

The presence of benzoic acid,[4] oakwood tea,[5] hydroxylamine[6] or a salt of tin[7] in copper baths causes an improved deposit. Boric acid[8] produces a smoother and less brittle deposit of nickel. Extract of licorice root[9] improves the deposit of zinc.

Gelatine or glue[10] in a solution of lead fluo-silicate and free fluo-silicic acid gives dense non-crystalline deposits which are commercially valuable. Without addition substances, loose

* Thesis submitted to the faculty of Indiana University for the degree of Master of Arts in Chemistry, by O. Ralph Overman.

[1] McMillan, "Treatise on Electro-Metallurgy" (1890) 9 and 196. Watts, "Electro-Deposition" (1889) 228.

[2] Langbein, "Electro-Deposition of Metals" (1898) 258.

[3] Watts, "Electro-Deposition" (1889) 342.

[4] Metal Industry (1903) 179.

[5] Trans. Am. Elect. Chem. Soc., 8, 83.

[6] Trans. Am. Elect. Chem. Soc., 6, 29.

[7] Berg und Huttenmann. Zeit. (1885) 249.

[8] Watts, "Electro-Deposition" (1889) 295.

[9] Tucker and Thomssen, Met. Chem. Eng., 7, 273 (1909).

[10] Betts, U. S. Pat. 713,278. Met. Chem. Eng., 1, 407 (1903). Uhe, Eng. and Min. Jour., Oct. 11, (1902).

crystal are formed, similar to those obtained from nitrate or acetate baths. Glue or gelatine,[11] however, when added to nitrate or acetate baths, does not give good deposits. So it seems that the fluo-silicic acid has some specific effect upon the deposition, and that the character of the deposit is not altogether due to the addition substance.

Organic colloids used in a lead perchlorate bath give smooth non-crystalline deposits.[12]

It has been found that a solution of lead perchlorate containing some free perchloric acid and a small amount of some substance as glue, tannin, licorice or, preferably, peptone is an excellent electrolyte for plating or refining. Thick, smooth deposits of high density may be obtained.[13]

The object of this research was to make a systematic experimental study of the effect of as large a number of addition substances as possible upon the character of electrolytic lead deposits. An attempt was made to classify the different substances and then to test these different classes.

Preparation of Materials.

The perchloric acid was made from sodium perchlorate,[14] from barium perchlorate[15] or from potassium perchlorate.[16]

Beakers were used as electrolyzing vessels.

The lead for anodes was cast in a graphite mold. Each anode was suspended by a copper wire which was cast into it. Two anodes were used in each beaker. A cathode of thin sheet copper 5 cm. square was placed between the two anodes.

The solutions were stirred at all times by a slow current of air. The apparatus[17] was so arranged as to give a slow but constant circulation of the liquid from the bottom of the beakers to the surface.

The air pressure[18] was furnished by a suction pump.

The composition of the solutions was about 6 percent of lead and about 4 percent of free perchloric acid.

[11] Senn, Z. Electrochem., April 14, 1905; Electrochem. and Metall. Ind., **3**, 272 (1905).
[12] Siemens and Halske, Ger. Pat. 223,152. J. S. C. I. **29**, 960 (1910).
[13] Mathers, U. S. Pat. 931,944. These Transactions, **17**, 261 (1910).
[14] Mathers, Jour. Amer. Chem. Soc., **32**, 66 (1910).
[15] Mathers and Germann, Trans. Amer. Electrochem. Soc., **19**, 71 (1911).
[16] See Appendix—"Preparation of Perchloric Acid," by F. C. Mathers. Page 331.
[17] Adapted from A. C. Cumming, Trans. Faraday Soc., **6**, 10 (1910).
[18] Ostwald's, Physico-Chemical Measurements (1894) 189.

Experimental.

A great variety of addition substances was used. In each case 0.2 gm. was first added, or, if the substance was a liquid, 4 drops were used. The bath was then electrolyzed with a current density at the cathode of 0.8 ampere per sq. dm. The electrolysis was continued for about twenty-four hours. If the metal which was deposited upon the cathode was unsatisfactory, the cathode was replaced by a new one and the amount of addition substance was doubled. The electrolysis was then continued for another twenty-four hours. If no marked improvement was then shown, the bath was discarded. If the deposit was good, the electrolysis was allowed to continue until the deposit began to show deterioration.

In presenting the data, the name of the addition substance is given, followed by a brief description of the character of the deposit. Unless the character of the deposit was changed by the increase in substance, no mention is made of it.

The volume of the bath was 200 c.c. in each case.

In each division the substances are arranged approximately in the order in which they showed the best action.

Inorganic Addition Substances.

Nitric acid: Very crystalline, much feathered on the edges.

Sodium arsenite: Exceedingly crystalline, poorly adherent.

Ammonium perchlorate: Two gm., very crystalline, feathered. The amount was increased successively to four, six and finally fifty gm. with no change except that the adherence of the deposit was decreased.

Aluminum perchlorate: Twenty c.c. of a concentrated solution, crystalline, feathered, dark colored, becoming poorer with increase of addition substance.

Magnesium perchlorate: Ten gm., crystalline, feathered, becoming worse with increase of addition substance.

Barium perchlorate or hydrochloric acid: Bad trees.[19]

Boric acid: 0.5 gm., very crystalline and feathered, becoming poorer with increase of addition substance.

Carbon bisulphide: Crystalline, slightly feathered on the edges.

Hydrogen peroxide: Very crystalline, feathered.

[19] Mathers, Trans. Amer. Electrochem. Soc., **17**, 271 (1910).

When 0.2 gm. of *peptone* was added to these baths a great improvement was observed in the character of the deposit.

Essential Oils.

Oil of cloves: Smooth, non-crystalline, firmly adherent. The deposition was continued in this bath for about 170 hours without increase of addition substance and with no deterioration in the character of the deposit.

Eugenol (chief constituent of oil of cloves): Smooth, non-crystalline, excellent appearance.

Oil of bay: Smooth, non-crystalline.

Oil of allspice or pimenta: Good, but slightly crystalline.

Oil of sassafras: Rough, crystalline.

Oil of citronella: Fair, improved with increase in amount of oil used.

Oil of orange: Smooth, but crystalline.

Oil of nutmeg: Crystalline, with needles on the edges.

Oil of caraway: Rough, crystalline.

Oil of eucalyptus: Rough, crystalline and slightly feathered.

Oil of cinnamon: Crystalline, poorly adherent.

Oil of cedar: Smooth in center, feathered along the edges.

Oil of peppermint: Crystalline, feathered.

Oil of aniseseed: Crystalline, irregular surface.

Oil of cade: Smooth, non-crystalline.

Oil of sandalwood: Good in center, edges feathered.

Oil of rosegeranium: Crystalline, slightly feathered.

Oil of cardamon: Rough, crystalline.

Oil of bergamot: Rough, irregular.

Oil of fennel seed: Smooth, crystalline.

Thymol, menthol, eucalyptol, methyl salicylate, cymene, oils of *pennyroyal, pine needles, savin, cajeput* and *artificial oil of lavender* each gave crystalline and feathered deposits.

Resins and Gums.

Gum guaiac: Slightly crystalline, striated, very firmly adherent.

Gum gambir: Smooth, adherent.

Catechu: Smooth, non-crystalline.

Phytolaccin: Crystalline, smooth, adherent, becoming less crystalline upon increase of substance.

Licorice: Smooth, non-crystalline.

Gum mastic: Smooth, crystalline.

Gum galbanum: Crystalline, feathered.

Asafoetida: Firm, peculiarly striated.

Gum camphor: Extremely crystalline, much feathered.

Succotrin aloes: Non-crystalline, firm, adherent, grown out in needles which on further electrolysis become club-shaped.

Gum benzoes: Crystalline, slightly feathered.

Burgundy pitch: Crystalline, grown out in needles.

Barbadoes aloes: Rough, non-crystalline, grown out in needles.

Balsam tolu: Very slightly crystalline, rough.

Gum tragacanth: Very crystalline.

Myrrha: Rough, adherent, non-crystalline.

Ammoniac: Crystalline, feathered.

Eucalyptus rostrata: Slightly rough, non-crystalline.

Pterocarpus marsupium: Slightly rough, non-crystalline.

Rubber (dissolved in chloroform): Crystalline, very much feathered.

Resinol: Crystalline, feathered, needled.

Gum gamboge, kauri gum, resin, macis, euphorbia: Crystalline, rough.

Gum damar, gum thus: Crystalline, feathered.

Sugars and Starches.

Glycogen: Smooth, only slightly crystalline.

Starch paste: Smooth, crystalline, becoming less crystalline with increase of addition substance.

Dextrin: Fairly good, adherent.

Levulose: Poorly adherent crystals, loosely feathered on the edges.

Dextrose: Crystalline, feathered edges.

Lactose: Crystalline, slightly feathered.

Maltose: Very crystalline, much feathered.

Mannit: Very crystalline, grown out in plates.

Dulcit: Crystalline, rough.

Raffinose: Crystalline, feathered.

Alkaloids and Their Derivatives.

Quinine sulphate: Crystalline, slightly feathered. After increasing the amount of addition substance, the deposit was firm, smooth and almost non-crystalline. Apparently the quinine underwent decomposition as an oily substance separated out on the surface of the liquid.

Morphine sulphate: Very crystalline, much feathered. Increase of substance reduced the amount of feathering.

Coniin: Very crystalline, much feathered.

Piperine: Crystalline, feathered.

Piperidine: Crystalline, with rough, feathered edges.

Piperazine: Crystalline, much feathered.

Glucosides.

Phloridzin: Smooth, almost non-crystalline, very good.

Garcinia Hamburii: Crystalline, smooth.

Amygdalin: Crystalline, feathered.

Salicin: Very crystalline, much feathered.

Convolvulus Scammonium: Very spongy, crystalline, irregular.

Proteids and Nitrogenous Animal Substances.

Peptone: Smooth, non-crystalline, adherent.

Glue: Fairly good, crystalline.

Isinglass: Crystalline, adherent.

Gelatine: Smooth, crystalline.

Hydrolyzed gelatine (warmed 14 hours on a water bath with dilute sulphuric acid): Crystalline, slightly feathered.

Hydrolyzed gelatine (warmed 14 hours on a water bath with water): Smooth, crystalline. Deposition was continued on one cathode for about 192 hours with very slight change in the character of the deposit.

Hydrolyzed gelatine (warmed 14 hours on a water bath with 10 c.c. of the electrolyte): Smooth, crystalline, not so good as the preceding.

Gelatine-peptones: Prepared[20] by heating 20 gm. of gelatin, 30 c.c. of water and 10 c.c. of perchloric acid (containing sulphuric acid) about 80 hours. This was cooled, and four or five

[20] Allen, "Commercial Organic Analysis," 4, 2d Ed., 470 (1898).

parts of absolute alcohol were poured in. The precipitate was filtered off, and filtrate was extracted with ether. The heated gelatine, the alcohol precipitate, the ether precipitate and the ether soluble portion were each used as addition substances. The ether soluble portion gave a fair deposit. Neither of the others was of any value.

Casein: Crystalline, feathered, feathering almost stopped upon increase of substance.

Casein (boiled with concentrated hydrochloric acid until the acid was evaporated out. The residue was extracted with ether, and the precipitate used as addition substance): Crystalline, slightly needled.

Creatine: Crystalline, slightly feathered.

Creatinine: Crystalline, feathered.

Avenin: Large, adherent crystals, but a smooth surface.

Egg albumin: Crystalline, very rough.

Ferments and Enzymes.

Pepsin: Smooth, non-crystalline.

Pancreatin: Slightly rough, but non-crystalline.

Diastase: Smooth, slightly crystalline.

Rennin: Crystalline, grown out in plates on the edges.

Phenols and Phenolic Substances.

Rosolic acid: Non-crystalline, but covered with parallel ridges. After a few hours this tendency to grow out in ridges ceases, but reappears with each fresh addition of the substance.

Hydroquinone: Crystalline, but firmly adherent and fairly smooth.

Pyrocatechin: Smooth, finely crystalline.

Resorcin: Crystalline, slightly feathered edges.

Orcin: Smooth, finely crystalline.

Tannin: Smooth, crystalline. An increase in the amount of substance caused the deposit to grow out in needles.

Pyrogallol: Smooth, crystalline, with rough edges.

Phloroglucin: Crystalline, fairly smooth.

Guaiacol: Crystalline, smooth. Becomes feathered when amount of substance is increased.

Picric acid: Very finely crystalline, feathered edges.

Gallic acid: Crystalline, feathered. Feathering ceases upon increased addition.

Para-nitro-phenol: Starts fairly well, but soon begins to feather out.

Phenol: Poorly adherent crystals, feathered.

Vanillin: Crystalline, a little feathered.

Metol: Crystalline, feathered.

Lacmoid: Very crystalline, much feathered.

Phenolphtalein: Crystalline, feathered.

Iodeosin: Extremely feathered, crystalline.

Miscellaneous.

Nitro-benzene: Smooth, non-crystalline, dark colored. A black oily substance separates out on the surface of the liquid.

Cochineal (prepared by warming the dried cochineal bugs with water, and filtering): Rough, fairly good.

Aniline: Smooth in center, crystalline, rough, feathered edges.

Furfurol: Rough, crystalline.

Agar agar: Rough, crystalline.

Antipyrine: Fairly smooth, slightly grown out in plates on the edges.

Methyl violet: Fairly smooth center, rough crystalline edges.

Indigo carmine: Smooth, very crystalline.

Blood serum: Smooth center, crystalline and feathered edges.

Azo-litmin: Edges feathered, prominent crystals.

Amido-aceto-phenone: Smooth center, crystalline, edges grown out in plates.

Asparginic acid: Very crystalline, large plates on the edges.

Phenacetin: Crystalline, feathered edges.

Cinnamic acid, chlorophyll, gelanthum, heliotropin: Crystalline, feathered.

Tereben: Crystalline, rough, feathered edges.

Benzaldehyde: Crystalline, feathered. Improvement shown when the amount of substance is increased.

Terpin hydrate: Crystalline, feathered edges.

Aluminum soap of castor oil: Crystalline, feathered, non-adherent.

Glycerine: Crystalline, non-adherent.

Mesitylene, urea, chloroform, cumol, collodion, pyridine: Very crystalline, much feathered.

Castor oil: Very crystalline, much feathered.

A few of the best of the addition substances were used in the lead fluo-silicate bath devised by Betts. These, with the character of the deposit, are listed below:

Oil of cloves: Smooth, almost non-crystalline.

Phloridzin: Smooth, almost non-crystalline; not so good as the above.

Gum guaiac: Rough, non-crystalline.

Peptone: Fairly good; shows some tendency to grow out in trees.

Glue: Rough, with some treeing.

Rosolic acid: Rough, non-crystalline, dark colored.

Oil of cade: Rough, crystalline, treed.

Gelatine: Rough, crystalline.

Avenin: Rough, crystalline.

Eugenol and phloridzin were used in a bath containing lead nitrate and nitric acid. Neither of them produced any improvement upon the deposit obtained in this bath when addition substances were not used.

In a few experiments, baths of 500 c.c. volume were used, to which the best of the addition substances were added. The addition substances used were: *Oil of cloves, gum guaiac, peptone, rosolic acid, oil of cade* and *phloridzin.* Two anodes were used in each beaker. A cathode of thin sheet copper five cm. square was placed between the two. The current density at the cathode was 0.8 ampere per sq. dm. An initial addition of 0.2 gm. of the solids and three drops of the liquids was made. Further additions of 0.05-0.1 gm. of the solids and 2-3 drops of the liquids were made every three or four days.

The electrolysis was continued for about seven weeks in the same baths, with only occasional short interruptions to allow the insertion of new anodes.

Oil of cloves, peptone, gum guaiac and *phloridzin* gave excellent deposits. The deposit from the bath in which oil of cloves was used was best of all. It was smooth, non-crystalline and very firmly adherent. The tendency to grow faster in some places than in others was very slight. There was absolutely no

tendency toward feathering. The color of the metal was very good. A total of 26 drops of the oil was added. The weight of lead deposited was 1,410 gm. The character of the deposit was still excellent when the experiment was discontinued.

One third of a c.c. of clove oil was used in the deposition of more than 1,410 gm. of lead, or about four pounds. Therefore, for one ton of lead about 166 c.c. (a little more than one-third of a pound) of the oil would be required.

The deposit from the bath containing peptone was non-crystalline and firmly adherent. It showed a slight tendency to bulge

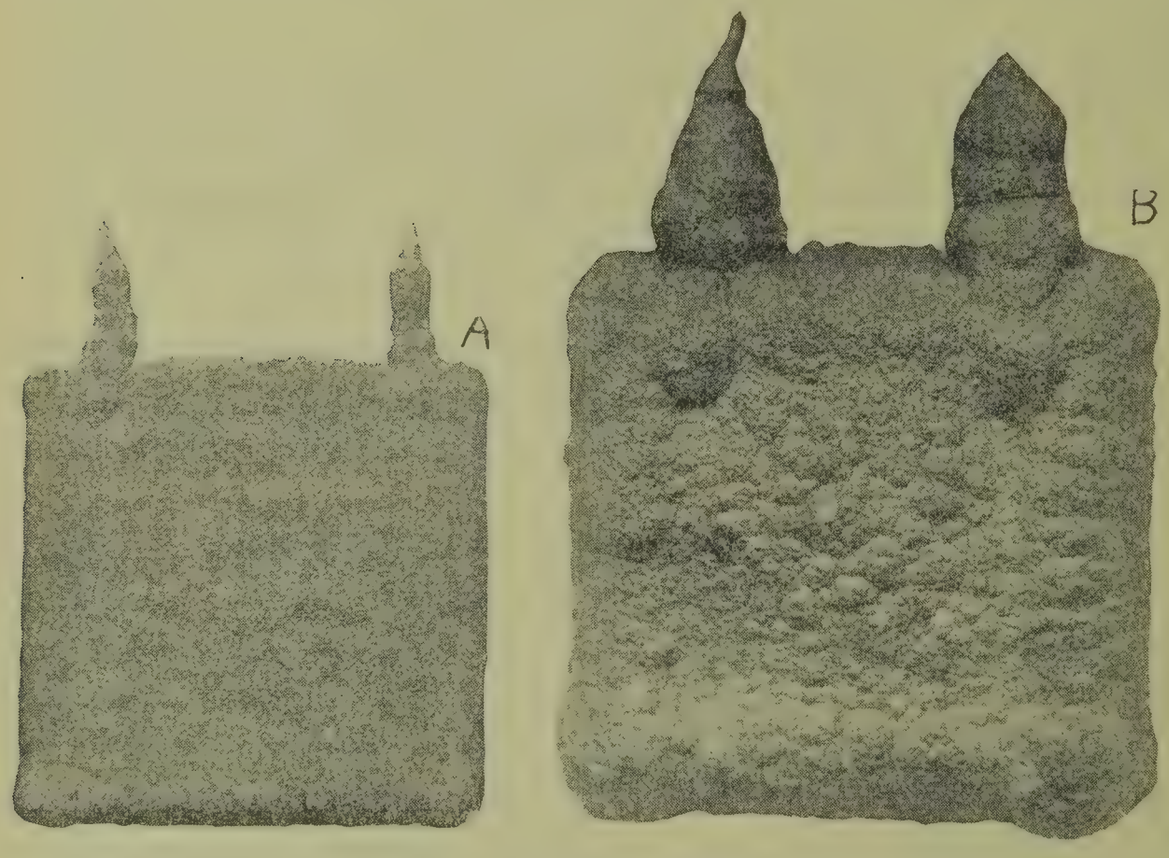

FIG. 1.

A. This cathode, which weighs 325 grams, was deposited in 216 hours, with the use of four drops of clove oil.

B. This cathode which weighs 3.13 lbs. (1410 grams), is 1 1/16 inches (2.6 cm.) thick. It was grown in a 500 cc. beaker. It is equal to any obtained from peptone. The total amount of clove oil used was 26 drops. The electrolysis extended over a period of two months.

in spots. About the same weight of lead was deposited as from the above bath; 0.75 gm. of peptone was used. The calculated weight of peptone per ton (900 kg.) of deposited lead is about five-sixths of a pound (350 gm.).

The deposit from the bath containing gum guaiac was non-crystalline. It showed a peculiar tendency to grow out in ridges,

but no tendency at all to feathering; 0.8 gm. of the gum was used. About the same weight of lead was deposited as from each of the above baths. So about eight-ninths of a pound (400 gm.) of the gum would be necessary for the deposition of a ton of lead (900 kg.).

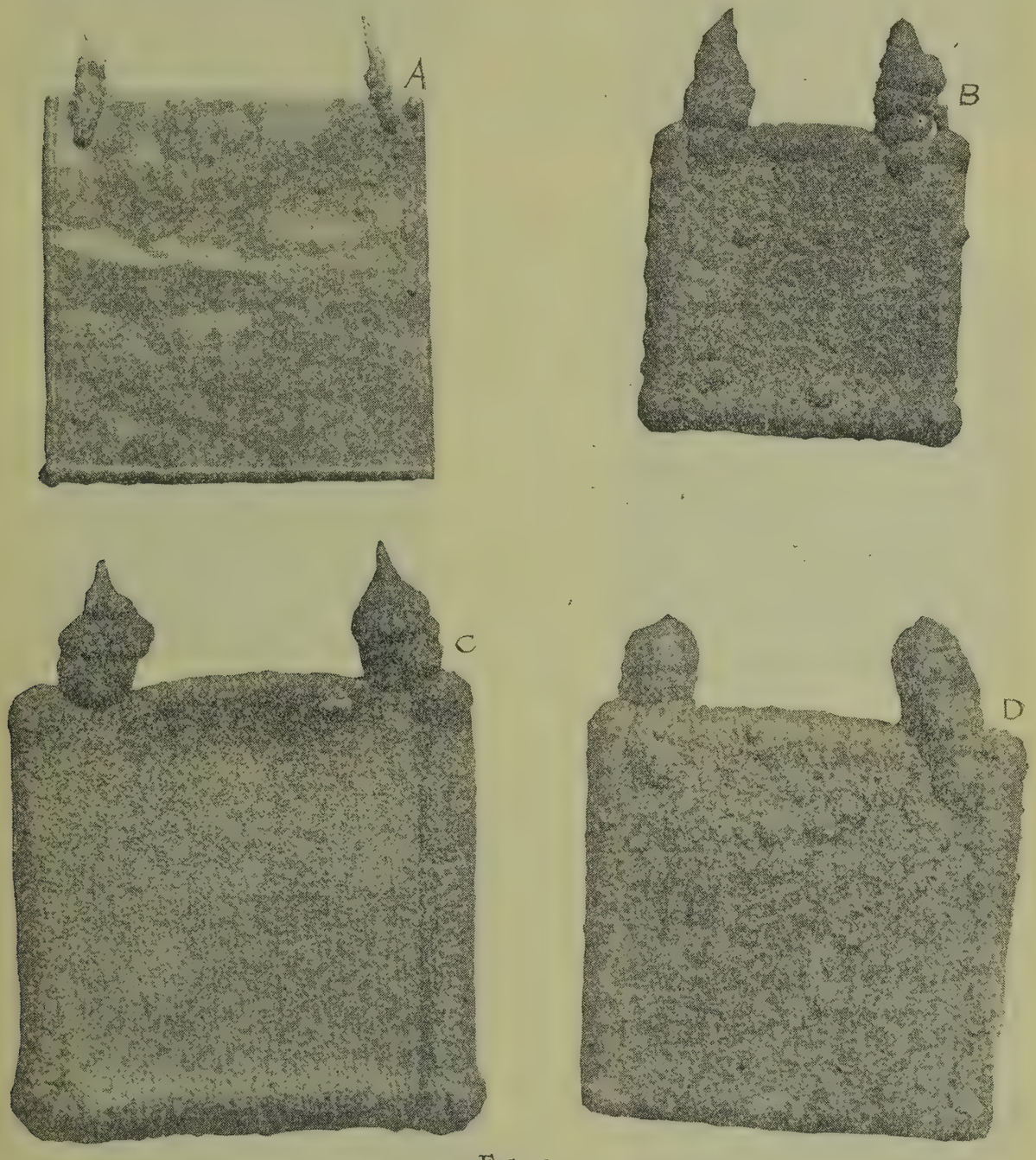

FIG. 2.

A. This cathode was made with peptone, which always gave good lead deposits.

B. This cathode is from a lead fluosilicate bath with the use of clove oil. . No other addition substances—and gelatine, peptone, oil of cade, gum guaiac and rosalic acid were tried—gave deposits which were equal to clove oil.

C. This was deposited from a 500 c.c. bath with the addition of 0.2 gm. gum guaiac. This addition substance will give good deposits if exactly the right quantity is used.

D. This cathode was deposited with 0.2 gm. of phloridzin. It was improperly cared for and slime, floating from the anode, has given it a roughened appearance. Phloridzin is one of the best addition substances although it is too expensive for commercial use.

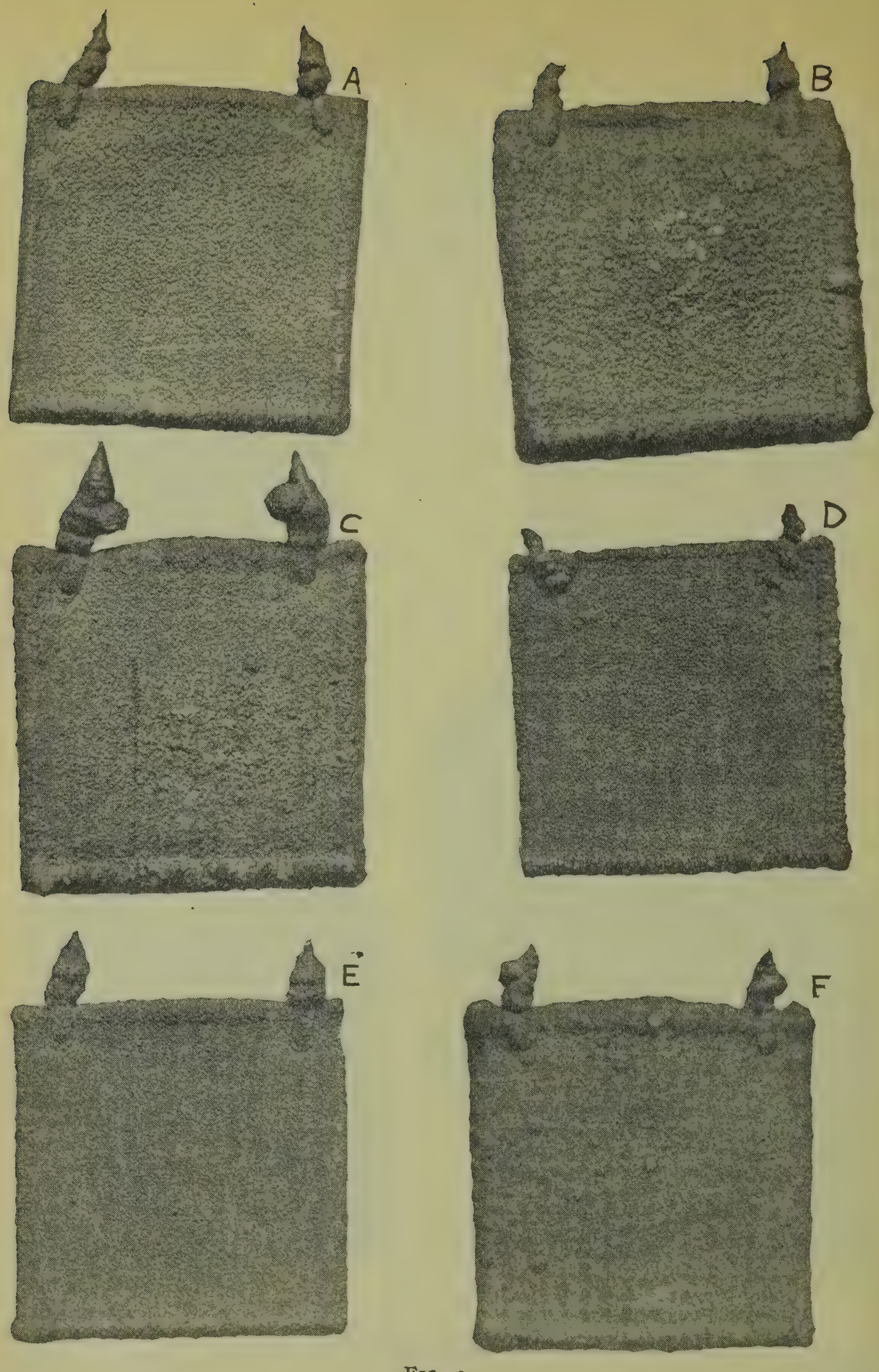

FIG. 3.

These cathodes are all of fair quality. They give an idea of the effects of some unusual addition substances.

A. Gum Gambier gave a deposit that is almost equal to the best. Many of the gums seem to contain substances, probably essential oils, which exert very powerful action as addition substances.

B. Catechu, an extract from wood, gave good deposits.

C. Quinine was the only alkaloid that seemed to have any decidedly beneficial action. It helped only after partial decomposition had taken place as shown by an oil upon the surface of the bath.

D. Cochineal gave a hard, dense but rough deposit.

E. Gelatine did not give good deposits from perchlorate baths.

F. Oil of citronella gave excellent deposits.

The deposit from rosolic acid was non-crystalline, but very deeply grooved and ridged. It showed some tendency to grow out in knobs, but did not feather. After about six weeks this bath was discarded.

The oil of cade did not do as well in the large as in the small bath. The deposit was adherent, but rough, and showed some tendency to short-circuit with the anodes.

The deposit from phloridzin was very good up to the time when it was discontinued, and gave promise of yielding an excellent cathode.

The amounts of oils indicated were added directly to the baths. The solid addition substances were dissolved in small quantities of water and filtered before being added to the baths.

The experimental data show that comparatively few of the substances gave deposits which might be commercially valuable. All of those which gave good deposits were organic. The best of these, approximately in the order in which they gave good deposition, were: *Oil of cloves* (or *eugenol*), *peptone*, *phloridzin*, *gum guaiac*, *licorice*, *phytolaccin*, *catechu*, *oil of cade*, *quinine*, *rosolic acid*, *starch*, *glycogen*, *pepsin*, *gum gambir* and *nitrobenzene*. *Oil of bay* and *oil of allspice* also gave very good deposits, but this was very likely due to the presence of *eugenol* in these oils.

As is shown in the above list, each of the classes of organic substances used is represented by one or more members which caused good deposition. The best of all, however, is oil of cloves, whose chief constituent, eugenol, is an unsaturated phenol of the formula $C_6H_3(OH)(OCH_3)(CH_2CH:CH_2)$. Eugenol, when used in small quantities as an addition substance, produces a very smooth, firmly adherent, non-crystalline deposit of excellent appearance and of high density.

Deposition of the best character does not occur until after several hours of electrolysis. This may be due to the presence of injurious impurities in the new bath, or to the fact that some decomposition product of the addition substance causes the good effect. After a period of time which depends upon the addition substance itself, the quality of the deposit begins to deteriorate. Then more of the addition substance must be added.

Rosolic acid and some of the gums produced very peculiar

vertically ribbed deposits, "as if molted metal had flowed down the cathode, solidifying on its way."[21]

Succotrin Aloes and certain other gums and extracts produce a peculiar growth of needle-like projections from the cathodes.

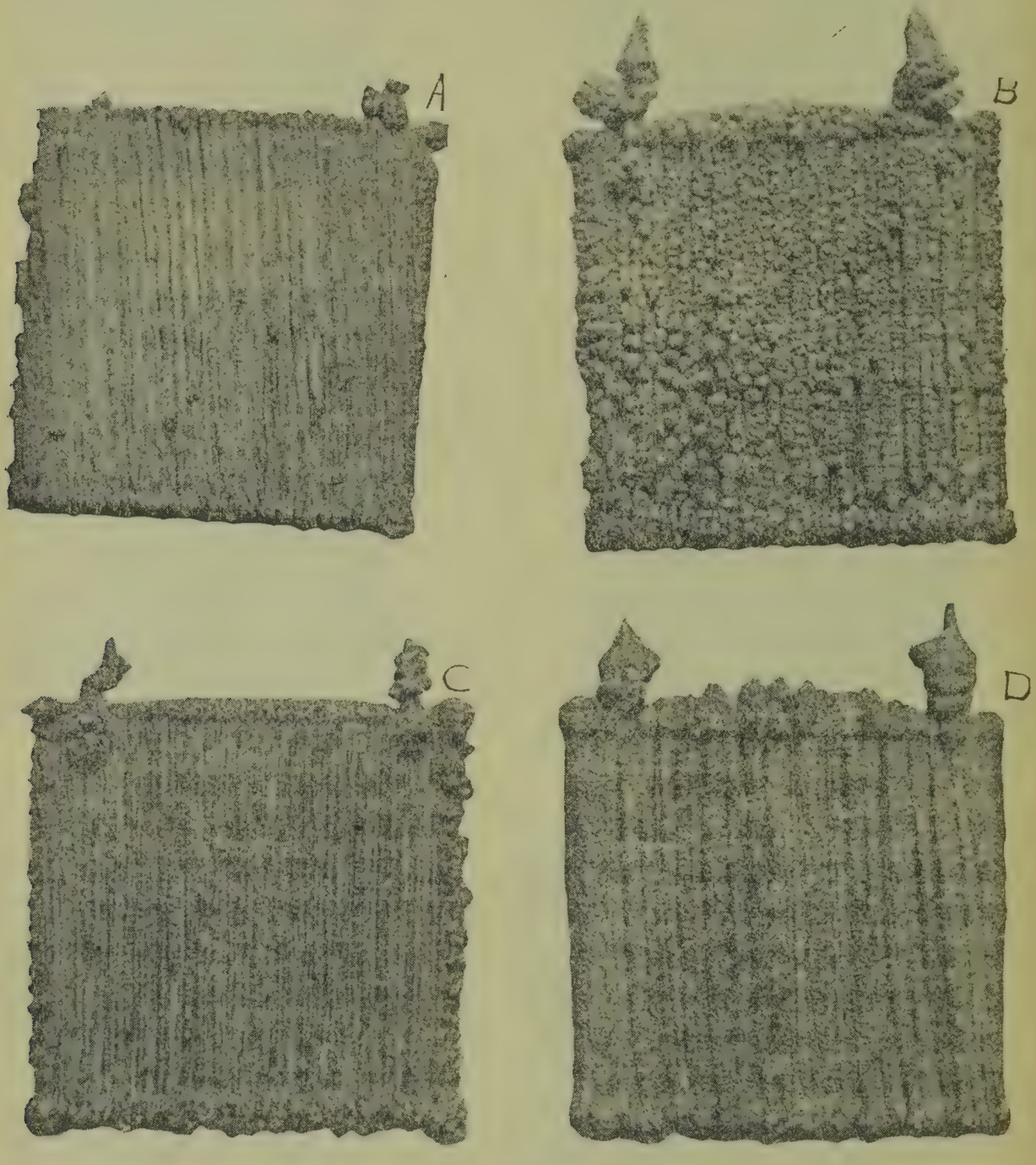

FIG. 4.

These pictures are given to illustrate the fact that addition substances may have the power to produce decidedly characteristic cathodes which are other than dense and smooth. A, B, C and D were from rosalic acid, asafoetida, antipyrine and gum guaiac. These addition substances always produce these vertically striated cathodes—especially when an excess of the addition agent has been used.

These phenomena show that different addition substances have distinct, different effects upon the deposited metal other than

[21] From a description of copper cathodes obtained from a copper sulphate solution that contained gelatine. Müller Zeit. Electrochem., 12, 317 (1906).

producing a smooth, dense, non-crystalline metal. Any theory to account for the action of addition substances must explain these three different kinds of deposits.

Many of the addition substances were changed during the

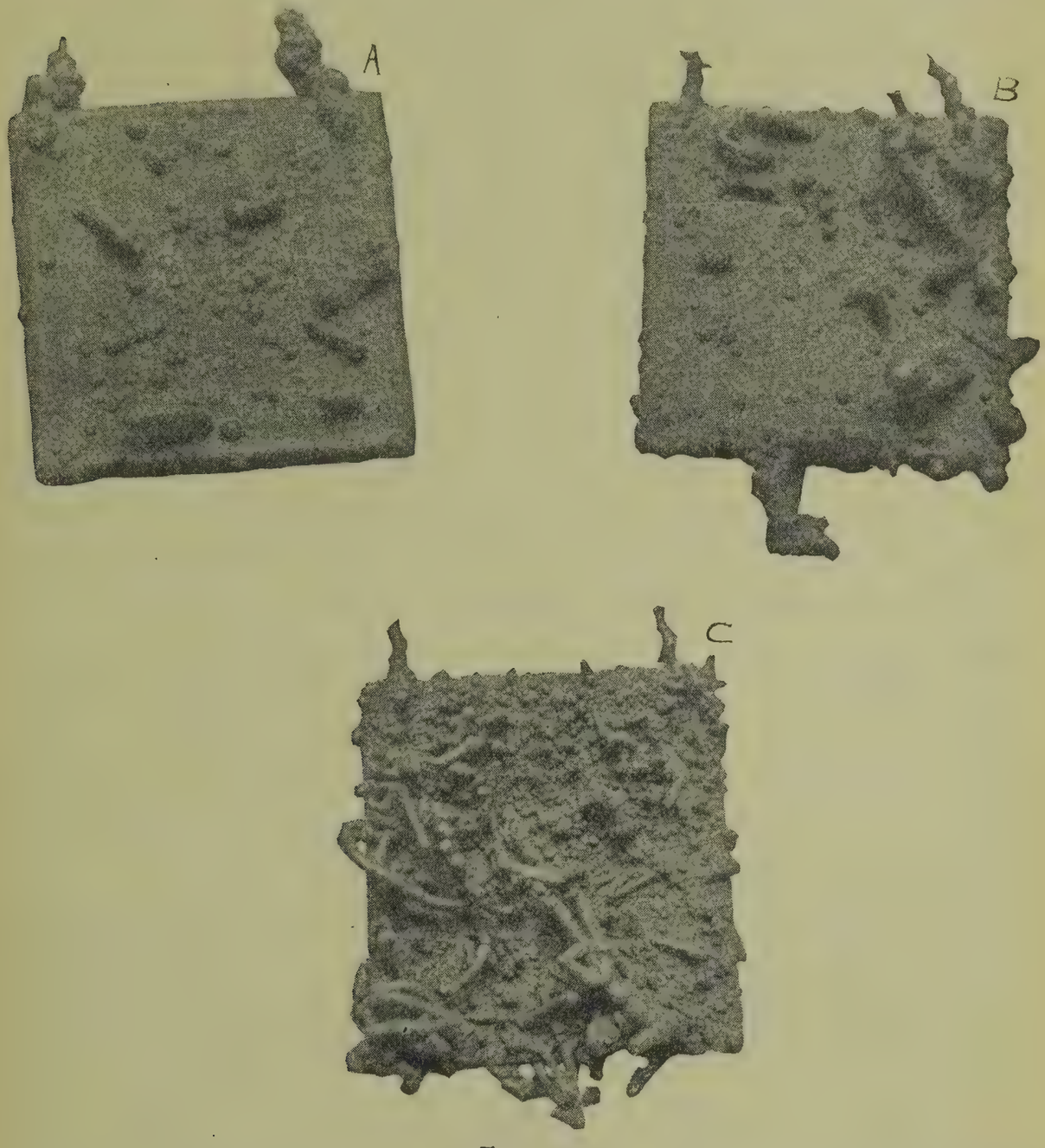

FIG. 5.

These peculiar wire growths are just as characteristic of these addition substances as are the striated deposits of the substances shown in Fig. 4. A, B and C were from licorice extract, succotrin aloe, and aloe barbados respectively.

electrolysis. *Rosolic acid* and some of the other colored substances changed color or lost their color. In many cases, precipitates were formed in the solutions. In one case *(quinine)*, an oily substance was formed, which floated upon the surface of the electrolyte.

Gum guaiac gave good deposits when used on a small scale and for a short period of time. In later and more extended experiments it was not very satisfactory.

Theoretical.

Several theories have been advanced to account for the effect of addition substances upon the electro-deposition of metals. Kern[22] made the statement, "That the greater the molecular weight of the addition agent and the larger the number of adjoiningly grouped hydroxyl (and amine) radicals which the compound contains, the more effective it is in producing denser, brighter, less crystalline and more coherent deposits of lead, copper and silver." This statement is based on the fact that in his experiments *pyrogallol* ($C_6H_3(OH)_3$) gave a better deposit than did *resorcin* ($C_6H_4(OH)_2$). In the experiments described in this paper, *eugenol* ($C_6H_3(OH)(OCH_3)(CH_2CH:CH_2)$), containing only one hydroxyl group and no amine group, produced far better deposits than substances rich in hydroxyl and amine groups, such as *pyrocatechin* ($C_6H_4(OH)_2$), *resorcin* ($C_6H_4(OH)_2$), *pyrogallol* ($C_6H_3(OH)_3$), *tannin* ($C_{12}H_3(OH)_3(COCH)_2$), or *aniline* ($C_6H_5NH_2$). However, *phloridzin,* containing five hydroxyl groups and having a large molecular weight (436), is one of the best addition substances. These facts agree exactly with the theory of Kern.

Another theory[23] is that the effect of the addition substances is due to their reducing action. It is true that some of the best addition substances are pronounced reducing agents. *Eugenol* and *phloridzin* readily reduce potassium permanganate. *Peptone,* however, produces only very slight reduction. *Gelatine, glue, pepsin* and *nitro-benzene* show little reducing action toward potassium permanganate. Some organic substances which are powerful reducing agents do not produce good deposition; *vanillin* is a good example of such a substance.

The presence of alkali, alkali earth or aluminum salts in the bath had a bad effect upon the deposits. This is contrary to the

[22] Kern, The Function of Addition Agents in Electrolytes. These Transactions, **15**, 441 (1909).

[23] Betts, U. S. Pat. 713,277. Met. Chem. Eng., **3**, 73 (1905).

general rule that more dense deposits are obtained from electrolytes containing alkali or alkali earth salts.[24]

Heretofore all the effective addition substances for lead baths have been colloids. Glue and peptone are the best examples. The author thinks that *phloridzin* and *clove oil* are not colloids. *Phloridzin*[25] is a glucoside that is obtained by extracting the root bark of apple, pear, plum or cherry trees with warm aqueous alcohol. Phloridzin crystallizes in silky needles which dissolve in cold water to the extent of 0.1 percent. The formula of phloridzin is $C_6H_7O(OH)_4.O.C_6H_3OH.O.C_6H_4CH.CH_3COOH$. The solubility is so small that attempts to determine the molecular weight by freezing-point method failed. No other experiment was tried to determine whether phloridzin acted as a colloid or not.

Clove oil was tested for colloidal action by observing its protective influence upon another colloid. One percent of glue in a solution will prevent the precipitation of lead chromate from solutions of less than 1/36 molecular concentration.[26] When 0.05 percent solutions of lead nitrate in saturated aqueous solutions of clove oil were mixed with an equivalent amount of potassium chromate in saturated[27] aqueous solutions of clove oil, the lead chromate was precipitated. The supernatent liquid had a more yellow color than when the precipitation was made in pure water. This difference in color might have been due to an oxidizing action upon the organic material by the chromate. Mixtures of lead nitrate and potassium chromate in clove oil and in solutions containing 2 c.c. of alcohol had the same color. Only a slight precipitate of lead chromate was obtained from 1 percent lead nitrate solution containing 0.5 percent of gelatine. These experiments show that if clove oil is a colloid, its power to prevent the precipitation of lead chromate is very feeble compared to that of gelatine. This protective action of colloidal substances was held[28] to be the cause of their effectiveness as addition sub-

[24] Kern. Trans. Amer. Electrochem. Soc., **15**, 473.

[25] Roscoe and Schlorlemmer, **3**, [5] 171 (1889).

[26] Free, Jour. Phys. Chem., **13**, 115.

[27] The saturated solution of clove oil was made by adding one c.c. of clove oil to 200 c.c. of water. This mixture was shaken vigorously at intervals for several hours and then allowed to stand over night. Apparently about one-third of the oil dissolved. This would indicate a concentration of about 0.25 per cent. The solution had an index of refraction of 1.33324, which represents a concentration of perhaps 0.2 percent, if calculated in terms of phenol or tannin. (A table of indices of refraction of aqueous solutions of clove oil was not at hand).

[28] Müller and Bahntje, Z. Electrochem., **12**, 317 (1906).

stances. Such a view is absolutely contrary to the fact that clove oil, a non-colloid, is the best addition substance for lead perchlorate baths.

It may be that electric endosmose will offer a satisfactory explanation for the phenomena of addition substances, but this theory was not tested in these experiments.

Attempts to find a relation between the chemical structure of the compounds and their action in the plating baths were unsuccessful. The only general statement is that the most helpful addition substances contain the hydroxyl group.

Summary.

This paper gives the results of experiments to find the best addition substances for use in lead plating and refining baths.

The following classes of compounds were tried: Inorganic, essential oils, resins and gums, sugars and starches, alkaloids and their derivatives, glucosides, proteids and nitrogenous animal substances, ferments and enzymes, phenols and miscellaneous substances.

Some compounds in all organic classes showed marked beneficial action. Most of the compounds were without marked beneficial action.

All effective addition agents contain the hydroxyl group. This is too general a relationship to be of any value.

The addition substances, arranged in the order of their beneficial action, are: Clove oil or eugenol, peptone, phloridzin and gum guaiac.

Clove oil is recommended for use in lead perchlorate plating and refining baths. About one-third of a pound is required per ton of lead.

Phloridzin is, perhaps, a slightly more satisfactory addition substance, but its cost is prohibitive for anything but experimental work.

Other satisfactory addition substances may be discovered among the oils and gums. These fields have not been completely covered.

University of Indiana,
Bloomington, Indiana.

Appendix.

PREPARATION OF PERCHLORIC ACID.[1]

By Frank C. Mathers.

Under the present market conditions, potassium perchlorate is the cheapest starting material for the preparation of perchloric acid. The only successful method is to distill with sulphuric acid under reduced pressure. About 60 c.c. of concentrated sulphuric acid should be used with each 100 gm. of potassium perchlorate. Less sulphuric acid than this, which is twice the amount required to form acid potassium sulphate, produces a residue in the flask which does not fuse at low enough temperature to give the best results. More sulphuric acid than this increases troublesome foaming. A pressure of less than 10 cm. of mercury should be maintained. Steam should be passed into the contents of the flask during the entire distillation at such a rate that no crystals (of $HClO_4.H_2O$) will form in the condenser. Only a small amount of steam is required, but an excess does no harm except to cause a little spattering and to lengthen the time of distillation. Without the addition of this steam (or water), decomposition begins soon after the distillation starts, and the yields are not above 70 percent. About 200 grams of potassium perchlorate is the maximum quantity which can be distilled rapidly from a 1,000 c.c. flask. The neck of the distilling flask should be lengthened to keep the rubber stopper away from the hot acid vapors. Care must be taken to prevent the contents of the distilling flask from sucking back into the steam flask. This is done by placing a stop-cock, which can be opened into the air, upon the steam flask. The yields of perchloric acid vary from 88 to 98 percent, depending upon how well the conditions of the experiment have been followed.

Sodium perchlorate should be the cheapest starting material for the preparation of perchloric acid, and this condition will exist if the demand for it should become very large. When this

[1] This is an abstract of a paper on "The Distillation of Potassium Perchlorate with Sulphuric Acid" which was published in "Indiana University Studies," Bulletin, 9, No. 12, p. 173 (1912). Copies of this bulletin may be obtained by applying to the Registrar, Indiana University, Bloomington, Indiana, or to the author of this paper.

condition arrives, the easiest and perhaps the most economical method to prepare perchloric acid will be to treat sodium perchlorate with an excess of concentrated hydrochloric acid (30 c.c. of hydrochloric acid to 20 grams of solid dry sodium perchlorate).[2] The sodium chloride which is formed is insoluble in the hydrochloric acid, and the perchloric and hydrochloric acids pass into the filtrate. By heating this filtrate to 135°, all the hydrochloric acid is volatilized and a solution of perchloric acid remains behind. Yields of 95 percent can be obtained.

Either of these methods will give a generous supply of perchloric acid for all experiments with perchlorate electrolytic baths.

University of Indiana,
Bloomington, Indiana.

DISCUSSION.

VICTOR ENGELHARDT (*Communicated*): The possibility of obtaining good deposits in the industrial refining of lead in electrolytic baths using oxydizing acids, in particular perchloric acid, as distinguished from the Betts refining process, was simultaneously discovered in America by Mathers and in Europe by Nussbaum, working in the electrochemical division of the Siemens & Halske Company, in Berlin, which division is under my superintendence. The process was patented by both parties; and in this connection it may be remarked that the German patent of Siemens & Halske is not No. 223152 (as was stated in the advance copy of Mr. Mathers' paper), but No. 223668. There seems to be confusion here. The Hagener Accumulator Works in Hagen, which has worked up this subject together with Siemens & Halske, has a large experimental plant in operation, working this process.

Since, however, Messrs. Mathers and Overman, in their exhaustive investigations of the action of different additions, in particular, organic additions, cover the historical development

[2] Mathers, Jour. Amer. Chem. Soc., 32, 66 (1909).

of this field and also the theoretical side of the question, I believe it is of interest for me to refer to an older patent which has been overlooked by these authors. It is a U. S. A. patent, No. 832024, taken out by Mr. Nussbaum and assigned to Siemens & Halske. In this patent, issued in 1906, it was first disclosed that, in metal refining by electrolysis, all those colloids work favorably which migrate to the cathode. This patent contains, besides, an attempted explanation of this phenomenon offered by me. In all electrolytic deposits which tend toward crystal or knob formations, the deposits on the corners and edges tend to become irregular because they automatically increase the current density at those points. In consequence of this the colloids present migrate in increased amount to just those places, producing a sort of local diaphragm action, which is continually changing its locality. One could in this respect speak of a wandering diaphragm action, changing its place continually to that of the highest current density. It would therefore be of great interest if the author would test the different organic additions used by him for their difference of migration directions, in order to determine whether there exists a connection between the direction of this migration and the perfection of the cathodic lead deposit.

(Translated by J. W. Richards.)

Prof. W. D. Bancroft (*Communicated*): Mr. Mathers has collected a mass of data and it is to be hoped that he will now go over the material carefully and systematically. When he does this, he will modify some of his statements. He says that glue or gelatine does not cause good deposits when added to a lead nitrate or lead acetate bath, and that therefore the good effect in the lead fluosilicate bath is due to something specific about fluosilicic acid. If the lead acetate solution is made as strongly acid as the lead fluosilicate solution, glue or gelatine does cause a good deposit. The specific effect is that of the gelatine. The ill success which Mr. Mathers had with aluminum perchlorate is undoubtedly due to faulty experimental conditions, because we have found a beneficial effect due to ferric acetate in a lead acetate solution.

Mr. Mathers concludes that good deposits are not caused by colloids because clove oil, a non-colloid, is the best addition sub-

stance for lead perchlorate baths. The conclusion is based on the author's unknown definition of a colloid. He adds that "it may be that electric endosmose will offer a satisfactory explanation for the phenomena of addition substances, but this theory was not tested in these experiments." This is quite unintelligible, because Müller and Bahntje have shown that colloids act only when they are carried to the cathode. One cannot have either electrical endosmose or cataphoresis (which is what Mr. Mathers really means) without a dispersed phase, in other words without a colloid.

The whole matter is quite simple if one defines one's terms. An effective addition-agent forms a dispersed phase, solid or liquid, which is carried to the cathode by the current and is adsorbed by the precipitating metal. We cannot predict the amount of adsorption in this case any more than we can as yet in cases involving no electrolytic precipitation, and consequently we cannot predict that clove oil will be more effective than gelatine with lead. We cannot even be certain that clove oil will be more effective than gelatine with other metals. We know that it is not as effective as gelatine in suspending lead chromate. The fault is in our theory of adsorption and not in our theory of electrolytic deposits.

It should be noticed that this definition excludes sodium chloride from the list of addition-agents. There is no more reason to call sodium chloride an addition-agent for copper than to call potassium cyanide an addition-agent for silver. These substances do not form dispersed phases and are not carried as such to the cathode by the current. They act by cutting down the ion concentration and the hydrolysis, and by changing the corroding action of the solution on the metal or the salts of the metal. It is merely a source of confusion when two fundamentally different phenomena are grouped together.

Mr. E. B. Spear: I think a great deal of work is required to be done on organic colloids before we can place the true causes very well. I have been working for a couple of years on this problem, and I have a paper partly written that I hope to present at the International Congress of Chemistry in the fall, on the "Effect of the Addition of Agents." We are continuing our work with the use of the ultra-microscope in order to ascertain what takes

place during the deposition. The great difficulty is that it is so hard to get pure water devoid of colloids.

MR. FRANK C. MATHERS (*Communicated*): The theory of Mr. Engelhardt, that the addition substances produce a sort of diaphragm, will not explain the formation of cathodes having club-like projections or vertical ridges.

Müller and Bahntje (Z. Electrochem., **12**, 319) gave just one experiment showing that gelatine in acid solution goes to the cathode, and in alkaline solution goes to the anode. Foerster had previously shown that egg albumen acted in the same way. I think that Bancroft's statement is too broad when he says "Müller and Bahntje have shown that colloids act only when they are carried to the cathode." Now, Müller and Buchner (C. A., **4**, 1928; from Z. Electrochem., **16**, 93) say that the colloids gelatine, starch, gum arabic and albumen greatly assist in the formation of firm, closely adhering coatings of calcium hydroxide upon cathodes, as shown by the reduced rate of reduction of sodium hypochlorite. This shows that the colloids glue and albumen, which are supposed to go to the anode, according to experiments, when the solution is alkaline, have an effect upon the cathode deposits in the alkaline solutions. How does the endosmosis and adsorption theory explain these experiments?

Large amounts of glue (1 percent) in lead acetate and acetic acid solutions (Bancroft, this volume, page 236) will give fair deposits except for rough edges which would prevent the production of thick deposits. Many of the addition substances mentioned in this paper produced excellent deposits if the experiment was continued for only a short time, but only a few of the addition substances would give good thick deposits. I think that glue in acetate solution belongs to the former division.

The statement that the good deposits with glue and fluosilicic acid were due to some specific power of the latter, because glue and acetate or nitrate did not give good deposits, was taken from work by Senn (Electrochem. and Metall. Ind., **3**, 272 (1905); from Z. Electrochem., April 14, 1905). I was inclined to believe that Bancroft was right and that the acidity of the solution was the important thing, but recent experiments, which I am not ready to describe at this time, have given excellent deposits of lead from solutions which reacted alkaline to litmus.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE EFFECT OF VARIOUS SUBSTANCES ON THE RATE OF CORROSION OF IRON BY SULPHURIC ACID

By Oliver P. Watts.

In Vol. 8 of the transactions of this society, C. F. Burgess called attention to the remarkable reduction in the corrosion of iron by sulphuric acid, brought about by the addition of a small amount of arsenious oxide to the acid. Later[1] he explained the protective action as follows: "The explanation which has been offered for this phenomenon is that the iron receives, by contact with the solution, an extremely thin coat of arsenic which resists the action of the acid and protects the underlying metals." He also gave experimental proof that the iron was coated with arsenic.

It has long been known that by dipping clean iron into solutions of suitable composition and concentration thin coatings of gold, silver, platinum, copper, and several other metals may be deposited on the iron. It is generally conceded that such coatings are not sufficiently continuous and impervious to protect the underlying metal from corrosion, even though the metal forming the coating may itself be thoroughly resistant to the corrosive agent. Instead of being a protection, such coatings are usually considered to be stimulators of corrosion.

Since all metals which thus deposit upon iron when it is immersed in a solution of the metallic salt are electro-negative to iron, a short-circuited voltaic cell is formed, of which the iron is anode and the metal deposit is the cathode. So long as any iron remains in contact with the electrolyte, it would seem, except for certain considerations which will be presented later, that the corrosion of the iron ought to be stimulated by this condition, and that the only way in which such a coating could afford good

[1] For references see list at end of paper.

protection would be by covering the iron completely, so that no electrolyte could come in contact with it.

Speaking of the effect of other metals in contact with iron, W. H. Walker says,[2] "Tin is a metal which, like copper, accelerates the corrosion of iron by aiding in the oxidation of the hydrogen set free by the reaction." M. P. Wood[3] calls attention to the injurious action of metals, "The use of anti-corrosive, or anti-fouling paints, containing salts of any metal, is attended with the greatest danger to the coated (iron or steel) structure. These pigments are extremely sensitive to the presence of saline elements in moisture, their action being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way."

It appears then, that arsenic is unique among the metals which precipitate themselves upon iron from solution, for arsenic protects iron almost completely from powerful corrosive agents, while the other metals are generally considered to aggravate corrosion and rusting. The protective action of arsenic cannot be due to any superior power of resisting attack by sulphuric acid, for silver, platinum and gold are even more resistant, and yet accelerate the corrosion of iron. It is evident that these other metals do not form continuous and impervious coatings over the iron, else they would protect it. It is difficult, perhaps impossible, even with the aid of the electric current, to deposit from solution a thin coating of one metal upon another so perfectly as to protect the underlying metal from corrosion by an acid ordinarily capable of attacking it. It is almost incredible that a thin yet perfect and non-porous metallic coating should be deposited by a process which depends for its operation upon the dissolving of the underlying metal. The protective action of coatings of copper, silver, etc. thus deposited on iron is about as effective as would be expected from a knowledge of their method of formation. They are continually being undermined by the corroding of the iron anode at points not yet covered, until the copper or silver becomes detached, to have its place taken by

a new coating, and so on, as long as any of the salt of the depositing metal remains in the solution. If the coated metal be removed to an acid, the corrosive action is similar, except that the renewal of the coating can take place only at a rate not greater than that at which the detached metal redissolves in the acid.

If the coating of arsenic is so porous and imperfect as the action of acids shows the coating of copper, for example, to be, how can the arsenic protect the iron any better than copper does? It occurred to the writer that the explanation lay in a high overvoltage or excess potential of hydrogen on arsenic, and the experiments which follow were undertaken to discover whether this is the explanation of the singular and mysterious protective action of arsenic. If the above explanation is correct, among the metals which deposit upon iron when it is immersed in a solution of their salts those having a high overvoltage for hydrogen should protect iron, and those of very low overvoltage should aggravate corrosion.

If an electrode of platinum coated with platinum-black be immersed in normal sulphuric acid the electrode will be electronegative to the solution by about 1.14 volts. If now a small but slowly increasing electromotive force be applied between this electrode and an insoluble anode it will be found that the platinized cathode becomes progressively electronegative with regard to the solution. When a certain difference of potential between the cathode and the solution is reached, bubbles of hydrogen begin to appear on the cathode. If a cathode of smooth platinum is used, hydrogen will not appear on this until it has become 0.09 volts more positive than the other cathode was when hydrogen first appeared on it. Similarly zinc must be 0.70 and mercury 0.78 volts more positive than the platinum-black before hydrogen appears upon them. This excess of potential required to cause a visible liberation of hydrogen upon a cathode of any particular metal, over the potential required for the liberation of hydrogen upon platinum coated with platinum-black, is known as the overvoltage of hydrogen upon that metal. In Table I are given the single potentials in normal solutions of the sulphates of the metals, and the overvoltage of hydrogen as stated by different observers.

TABLE I.

	Single Potential	Overvoltage in normal sulphuric acid			In 5 per cent. KOH.
		Caspari[4]	Foerster[5]	Harkins[6]	Nutton and Law[7]
Mercury	—0.98	0.78	0.43	0.74	
Zinc	+0.524	0.70		0.71	0.70
Lead	—0.095	0.64	0.35	0.62	0.57
Tin	—0.085	0.53	0.43	0.55	0.61
Cadmium	+0.162	0.48	0.48		0.52
Arsenic	—0.550			0.39	
Bismuth	—0.490			0.38	
Iron	+0.093				0.15
Copper	—0.515	0.23	0.10	0.25	0.41
Cobalt	—0.019			0.22	
Nickel	—0.022	0.21	0.10	0.15	0.37
Silver	—0.947	0.15		0.13	
Platinum	—1.140	0.09	0.07	0.07	
Gold	—1.356	0.02	0.055		

On the theory that the protection of iron by a deposit of arsenic is due to the high overvoltage of hydrogen on the latter the action would be as follows: Iron dissolves and by so doing deposits arsenic upon the surface of the iron. Since the arsenic is deposited simultaneously with the dissolving of the iron, and only as a result of this dissolving, it is hardly possible that the iron should be perfectly covered by arsenic, but here and there holes will exist, allowing the iron to make contact with the electrolyte. Voltaic cells are thus formed. From the single potentials of iron and of arsenic, + 0.093 and — 0.550, these cells should have an electromotive force of 0.64 volts, and the corrosion of the iron ought to be very vigorous. It is here that the overvoltage of hydrogen comes in play. The iron is anode and the arsenic cathode, and, just as in any other primary cell with sulphuric acid as electrolyte, hydrogen is deposited on the cathode. But when hydrogen is liberated on arsenic the potential of the latter is raised 0.39 volts higher than — 0.277, the potential at which hydrogen is liberated on platinum-black. This would raise the potential of the arsenic to + 0.113 volts, or higher than the potential of the iron anode. This means that in our iron-arsenic cell there can be no visible evolution of hydrogen on the arsenic, for before this can occur the potential of the cathode has become equal to that of the anode, and corrosion of

the iron ceases, in other words, this particular primary cell polarizes so badly that after a few seconds of action its electromotive force has fallen to zero.

If the above explanation is correct, protection should be afforded by those metals which plate out on iron by immersion, and whose overvoltage for hydrogen is great enough to raise their potentials to at least equal the single potential of iron. The potentials of the following metals are far enough below that of iron to expect that they will deposit on iron even in moderately strong sulphuric acid: antimony, arsenic, bismuth, gold, lead, mercury, platinum, silver and tin. Potential measurements made by students in the writer's laboratory indicate that chromium should be included in the list. Omitting lead, on account of the insolubility of its sulphate, mercury, tin, and arsenic show the highest overvoltage; compounds of these metals were therefore used in a preliminary experiment, by A. C. Shape.

Specimens of mild sheet steel of 22 gauge, 5 centimeters square, were pickled in sulphuric acid to remove the scale, dried, weighed, and corroded in sulphuric acid to which three volumes of water had been added. The amounts of the reagents added were 4 c.c. of twice normal stannous chloride, the same volume of twice normal sodium arsenate, and 16 c.c. of half normal mercuric chloride. The results are shown under Test 1.

Test 1.

Specimen	Reagent Added	Original Weight	Loss	
			In 24 Hours	In 48½ Hours
A	None	16.38 g.	6.64 g.	10.32 g.
B	$SnCl_2$	16.53	0.09	0.11
C	$HgCl_2$	16.48	0.42	1.37
D	Na_3AsO_4	16.93	0.07	0.10

Tin and arsenic gave equal and excellent protection, but the action of mercury was not so satisfactory. The failure of the mercury may have been due to its gathering in drops and leaving exposed considerable areas of the iron. It has been pointed out by Cushman[8] that the protective action of a piece of zinc in contact with an iron surface extends but a very short distance from the zinc. The corrosion of specimen *C* was very peculiar, and was confined to deep pits about the diameter of a pin. The pitting was especially noticeable upon the edges of the sheet. In view

of these facts, the writer did not consider the imperfect protection afforded by mercury to be fatal to his theory as to the nature of the protective action, and he decided to investigate the matter more fully.

The specimens used were as previously described. Corrosion was carried out in covered glass tumblers containing 200 c.c. of solution. The acids used in the following tests were sulphuric acid of specific gravity 1.140 at 15°C. corresponding to 19.6 percent acid, and of specific gravity 1.072 or 10.48 percent acid, hydrochloric acid of specific gravity 1.095 or 18.8 percent and hydrobromic acid of specific gravity 1.145 or 18 percent acid. In future these acids will be referred to by their approximate percentage composition.

In Test 2 the reagents added were in such amount as to make the solutions one hundredth normal with regard to the reagents. Since antimony is closely related chemically to arsenic, it was hoped that this might give the same degree of protection, and, on account of its less poisonous nature, prove useful commercially for this purpose.

Test 2.

For 21 h. 45 m. at room temperature (21°C.)

Specimen	34.9 per cent. H_2SO_4	Reagent Added	Weight	Loss
1	"	None	16.08	11.50
2	"	$Ni(NH_4)_2(SO_4)_2$	16.42	12.25
3	"	$CuSO_4$	16.12	11.36
4	"	$AgNO_3$	16.59	11.37
5	"	$Sb_2(SO_4)_3$	16.44	12.15

On examining the specimens at the end of the time specified they were all found to be covered with crystals of ferrous sulphate to such an extent that further corrosion was prevented. To avoid this difficulty weaker acids were used in all other tests.

Test 3.

In 19 percent sulphuric acid for 24 hours.

Specimen	Reagent Added		Weight	Loss
6	None		16.13 g.	5.47 g.
7	0.75g Na_3AsO_4	=0.20g. As	16.52	0.08
8	$As_2(SO_4)_3$	=0.20g. As	16.61	0.02
9	$SnCl_2$	=0.47g. Sn	15.92	0.02
10	0.678g. $HgCl_2$	=0.50g. Hg	16.14	1.40

The results of this test in the more dilute acid confirmed those of the previous test, except that the mercuric chloride showed less protective action.

In Test 4 various additions were made to the acid. As in Test 3 the various solutions were one twenty-fifth normal as regards the metallic salts added.

Test 4.

In 19 percent sulphuric acid for 20 hours 15 minutes.

Specimen	Reagent Added	Weight	Loss
11	None, No. 11 was amalgamated.....	15.88	6.36
12	$Co(NO_3)_2$	14.87	9.87
13	$Bi_2(SO_4)_3$	15.79	14.36
14	$Sb_2(SO_4)_3$	16.39	8.67
15	K_2CrO_4	16.21	12.40
16	$HgNO_3$	16.20	13.61
17	$Cr_2(SO_4)_3$	16.04	2.21
18	$CuSO_4$=0.47 g. Cu	16.06	13.96
19	$AgNO_3$=1.617 g. Ag	16.31	16.31+

Specimen No. 11 was thoroughly amalgamated. At the end of 15 hours it was found that No. 19 had completely dissolved. Only one reagent, chromium sulphate, showed any protective influence. Silver nitrate, bismuth and copper sulphates and potassium dichromate accelerated corrosion. The effect of antimony sulphate, cobalt nitrate and of amalgamation is in doubt. A few hours from the start much spongy silver had collected in the solution and on the iron of No. 19, metallic copper was evident as a powder in No. 18, and bismuth powder in No. 13. In No. 14 antimony was deposited on the iron in loosely adherent flakes, which peeled off from time to time. No silver nitrate remained in solution 19 at the end of the test. The insoluble residues left after removing the specimens were washed, dried and weighed. In 13, 14, 18 and 19 the residue was equal, within a few milligrams, to the weight of bismuth, antimony, etc., originally contained in solution, plus the amount of insoluble matter calculated for the iron dissolved in each case. Chromates and dichromates have often been recommended[9] for the prevention of the rusting of iron and steels when exposed to the air, or in sea water. The great increase in corrosion caused by the addition

of potassium chromate was therefore rather surprising. A comparison of No. 15 and No. 17 suggests that the protective action heretofore ascribed to chromates may really be due solely to the chromium which they contain, and not to the chromate as such. The marked increase of corrosion by mercurous nitrate is noteworthy.

It is stated by Burgess[10] that the protective effect of arsenic in hydrochloric acid is much less than in sulphuric acid, and Test 5 was arranged to learn the effect of several substances upon corrosion by hydrochloric acid.

Test 5.

In 19 percent hydrochloric acid for 24 hours.

Specimen	Acid	Reagent	Weight	Loss
20	19% H_2SO_4	None	15.92	13.92
21	19% HCl	None	16.46	1.89
22	" "	$CrCl_3$, about 3 g.....	15.99	2.42
23	" "	K_2CrO_4	16.55	1.91
24	" "	Na_3AsO_4 = 0.25 g. As.	15.82	0.13
25	" "	$SnCl_2$ = 0.59 g. Sn.	16.15	2.14

Hydrochloric acid dissolved about one-seventh as much iron as sulphuric acid. Potassium chromate has no effect on the rate of corrosion by hydrochloric acid, while stannous chloride and chromium chloride act as accelerators instead of retarders of corrosion.

Test 6.

For 24 hours.

Specimen	Acid	Reagent	Weight	Loss
26	19% H_2SO_4	None	16.03	7.84
27	19% HCl	None	16.43	1.83
28	19% H_2SO_4	N/25 $Bi_2(SO_4)_3$	15.93	12.13
29	" "	N/25 Na_2SnO_2 = 0.51 g. Sn.	15.98	0.68
30	" "	N/25 $Ni(NH_4)_2(SO_4)_2$	16.08	7.29
31	" "	N/25 $Sb_2(SO_4)_3$	15.97	4.86
32	" "	N/25 $KMnO_4$	16.45	15.14
33	" "	N/25 NaCl = 0.286 g. Cl....	16.45	4.01
34	" "	2 g. CrO_3	16.25	15.15
35	" "	2 g. chrome alum	16.00	8.81
36	" "	N/25 KNO_3	16.13	10.25
37	" "	5 g. CrO_3	15.47	15.47+

Specimen No. 37 was entirely dissolved at some unknown time during the test. Chromic acid, potassium permanganate, potas-

sium nitrate and bismuth sulphate are accelerators, sodium stannate, antimony sulphate and sodium chloride are retarders of corrosion, while nickel ammonium sulphate and chrome alum have little effect. The oxidizing agents in 32, 34 and 37 were reduced before the end of the test.

Since the previous tests had demonstrated that chromic acid and chromates do not render iron passive in sulphuric acid, the action of these and other oxidizing agents was tried in solutions of a neutral salt.

Test 7.

For 12 days, 16 hours.

Specimen	Reagent	Weight	Loss
38	29 g. NaCl + 10 g. CrO_3	15.96	1.99
39	26 g. NH_4Cl + 10 g. CrO_3	15.54	1.99
40	29 g. NaCl + 10 g. $KClO_3$	15.68	5.22
42	29 g. NaCl + 10 g. $KMnO_4$	16.21	3.71
43	29 g. NaCl + 10 g. $K_2Cr_2O_7$	15.97	0.065
51	Water + 10 g. CrO_3	15.91	0.005
52	29 g. NaCl	15.77	0.043

The addition of the oxidizing agents strongly stimulated corrosion, except in No. 43. This result needs confirmation by further experiments.

Test 8.

For 29 hours.

Specimen	Acid	Reagent	Weight	Loss
44	19% H_2SO_4	10cc HCl = 1.99 g. Cl...	15.88	0.70
45	19% HCl	None	15.86	1.65
46	19% HCl	About 10 g. $CrCl_3$	16.01	1.92
47	19% HCl	10 g. K_2CrO_4	16.02	7.82
48	19% H_2SO_4	10 g. NaCl = 6.1 g. Cl ..	15.72	0.32

Previous tests had shown that salt and other chlorides diminished the corrosion by sulphuric acid, and the writer expected that the increased amount of salt in No. 48 would still further diminish corrosion, but was not prepared for the astonishing result obtained in No. 44. Previous tests had shown that in 24 hours the sulphuric acid dissolved from five to seven times as much iron as the hydrochloric. Now the substitution of 10 c.c. of the hydrochloric acid for an equal volume of water in the

sulphuric acid reduces the corrosion to less than half that of hydrochloric acid.

Up to this time all experiments had been carried out upon the laboratory table, subject to whatever variations there might be in room temperature during the twenty-four hours. A study of the results showed that different tests were not comparable. All the tests which follow were carried out in a water bath maintained at 30° C.

Test 9.

In a water-bath at 30° C.

Specimen	Acid	Reagent	Weight	Loss	Time Hours
53	19% H_2SO_4	None	15.35	15.35+	20
54	19% H_2SO_4	22 cc. HCl = 3.98 g. Cl	15.78	0.93	24
55	19% H_2SO_4	5 g. NaCl = 3.06 g. Cl	15.70	1.24	24
56	19% H_2SO_4	None	15.65	14.92	22
57	10% H_2SO_4	None	15.75	6.62	24
58	19% HCl	None	15.74	5.06	24
59	19% H_2SO_4	None	15.14	14.84	22
60	19% H_2SO_4	5 g. KNO_3	15.63	15.63+	20
61	19% H_2SO_4	5 g. resorcin	15.84	10.36	24
62	19% H_2SO_4	5 g. hydrochinone	15.74	7.48	24

Specimens No. 53 and No. 60 were found to be entirely dissolved at the end of 20 hours, but how much earlier complete solution occurred is not known. A comparison of No. 53 and No. 54 shows that the restraining effect of chlorine is about the same, whether it is added in an acid or in a chloride. The reducing agents in No. 61 and No. 62 retard corrosion somewhat, but since an alkaline solution is needed to make them energetic reducers, it is hardly to be expected that they would have much effect in a strongly acid solution.

The lack of temperature control in previous tests tended to exaggerate differences in the rate of action of the various solutions, for the more rapid action of any solution at the outset gave it a higher temperature, which still further increased its rate of action. This is plainly seen in comparing the rates of corrosion by sulphuric and hydrochloric acids. Without the water bath, sulphuric acid dissolved six to seven times as much iron as hydrochloric acid, but with temperature control it dissolved only three times as much.

Test 10.

In water-bath at 30° C. in 19 percent H_2SO_4.

Specimen	Reagent	Weight	Loss	Time
63	3 g. K_2SO_4	15.78	15.78	24 hours
64	5 g. $(NH_4)_2SO_4$	15.81	15.81	24 "
65	5 g. NH_4Cl = 3.27 g. Cl	15.67	2.06	24 "
66	1 g. NH_4Cl = 0.67 g. Cl	15.77	10.28	24 "
67	5 g. KBr = 3.36 g. Br	15.62	0.24	24 "
69	1 g. $PbCO_3$	15.54	15.54+	22 "
70	None	15.22	15.22+	22 "
71	2 g. H_3BO_3	15.37	15.37	24 "
72	2 g. citric acid	15.34	15.15	24 "

Before twenty-two hours had elapsed No. 69 and No. 70 were dissolved. Potassium and ammonium sulphates, boric and citric acids, and the small amount of lead sulphate contained in its saturated solution, were without marked effect. Potassium bromide is a strong restrainer of corrosion, and ammonium chloride acts similarly, but far less effectively.

Test 11.

19 percent H_2SO_4 in water-bath at 30° C. for 20 hours.

Specimen	Reagent	Weight	Loss
73	0.94 g. $Na_3AsO_4 12H_2O$ = 0.25 g. As	15.44	0.53
74	0.47 g. $Na_3AsO_4 12H_2O$ = 0.125 g. As	15.32	0.77
75	0.094 g. $Na_3AsO_4 12H_2O$ = 0.025 g. As	15.80	13.62
76	0.016 g. $Na_3AsO_4 12H_2O$ = 0.004 g. As	15.81	14.56
77	1 g. $Na_2SnO_3 3H_2O$ = 0.44 g. Sn	15.80	1.29
78	0.5 $Na_2SnO_3 3H_2O$ = 0.22 g. Sn	15.74	2.44
79	0.1 $Na_2SnO_3 3H_2O$ = 0.044 g. Sn	15.63	4.43
80	0.05 $Na_2SnO_3 3H_2O$ = 0.022 g. Sn	15.84	7.18
80	2 g. $Na_2SnO_3 3H_2O$ = 0.89 g. Sn	15.73	0.68
82	None	15.74	15.13

The amount of sodium arsenate required for effective restraint of corrosion by 19 percent sulphuric acid lies between 0.47 and 0.09 g., or 0.125 and 0.025 g. arsenic, per 200 c.c. E. Heyn and O. Baur[11] find that 0.0069 g. As_2O_3 in 250 c.c. of 1 percent sulphuric acid diminishes the corrosion by one-third. Two grams of sodium stannate are required to produce equal protection.

In Test 12 the accelerating effects of copper, silver and platinum were compared, and also the relative corrosion by hydrochloric and nitric acids of about equal molecular strengths.

Test 12.

In water-bath at 30° C. for 24 hours.

Specimen	Acid	Reagent	Weight	Loss
83	10.5% H_2SO_4	Ag_2SO_4 = 0.2 g. Ag ...	15.73	8.15
84	10.5% H_2SO_4	Ag_2SO_4 = 0.1 g. Ag ...	15.49	7.50
85	10.5% H_2SO_4	Ag_2SO_4 = 0.02 g. Ag ..	15.61	5.06
86	10.5% H_2SO_4	$CuSO_4$ = 0.15 g. Cu ...	15.40	7.23
87	30% HNO_3	None	15.83	15.83+
88	19% HCl	None	15.88	7.78
89	10.5% H_2SO_4	$PtCl_4$ = 0.025 g. Pt	15.81	12.52
90	10.5% H_2SO_4	$PtCl_4$ = 0.075 g. Pt.	15.29	12.77
91	10.5% H_2SO_4	$HgSO_4$	15.33	4.43
92	10.5% H_2SO_4	None	15.80	5.89

Specimen No. 87 was attacked violently, and was entirely dissolved in a few minutes. The excessive activity of nitric, as compared with sulphuric or hydrochloric acid, can only be due to its strong depolarizing action in removing hydrogen from the iron. Silver and copper both accelerate corrosion, as was expected from the low overvoltage of hydrogen on these metals. Equal weights of metal show about the same effect, but in chemically equivalent quantities the effect of silver is much the greater. The small amount of silver in No. 85 seemed to diminish corrosion. Platinum had a tremendous effect at the start, and even at the end of the test was a more powerful stimulator than the other metals.

Test 13.

In 10.5 percent H_2SO_4 at 30° C. for 24 hours 15 minutes.

Specimen	Reagent	Weight	Loss
93	3 g. KI = 2.3 g. I	15.07	0.04
95	5 g. $K_2Cr_2O_7$	15.81	8.62
96	4 g. $MnCl_24H_2O$ = 1.43 g. Cl.....	15.17	1.34
97	2 g. KF = 0.65 g. F.....	15.84	3.46
98	20 cc. of 31% HF = 6.5 g. F.....	15.69	0.44
99	1 g. $Cr(OH)_3$ = 0.52 g. Cr.....	15.61	0.56
100	5 g. K_2CrO_4	15.45	8.17
101	None	15.76	5.55
102	4 g. chrome alum = 0.42 g. Cr.	15.81	3.88

The protective action of hydrofluoric acid and of potassium fluoride are nearly proportional to their fluorine content. The stimulative action of potassium chromate and dichromate is in striking contrast to the protection afforded by chromium sulphate. Chrome-alum is a much less efficient protective agent

per unit of chromium than chromium sulphate. These experiments indicate the possibility of a revision in our ideas of the manner in which chromates protect iron from rusting, and may lead to the substitution of chromium salts for the chromates heretofore used to render iron "passive."

Test 14.

In water-bath at 30° C. for 20 hours 45 minutes.

Specimen	Acid	Reagent	Weight	Loss
103	19% H_2SO_4	5 g. KI = 3.83 g. I.....	15.56	0.03
104	19% H_2SO_4	1 g. KI = 0.76 g. I.....	15.57	0.06
105	19% H_2SO_4	None	15.60	13.10
106	10.5% H_2SO_4	2 g. KNO_3	15.54	5.17
107	10.5% H_2SO_4	2 g. $KClO_3$	15.64	9.97
108	10.5% H_2SO_4	None	15.31	4.40
109	19% H_2SO_4	25 cc. of 18% HBr = 5.1 g. Br	15.29	0.31

Potassium iodide proves an excellent protective agent, and hydrobromic acid acts similarly. Of the two oxidizing agents, potassium chlorate stimulated corrosion much more than did potassium nitrate, as was to be expected from its larger amount of available oxygen.

Test 15 was made to compare the effects of very small additions of several metals. At the end of a few hours the specimens were removed, brushed, dried, weighed and returned to the acid.

Test 15.

In 19 percent H_2SO_4 at 30° C.

Specimen	Reagent	Weight	Loss at end of time in hours		
			2.25	5.72	8.3
110	5 g. $K_2Cr_2O_7$	15.27	3.06	5.71	15.27+
111	$PtCl_4$ = 0.016 g. Pt.....	14.88	6.76	8.85	14.88+
112	$AuCl_3$ = 0.016 g. Au	15.78	0.19	0.85	11.33
113	$Bi_2(SO_4)_3$ = 0.020 g. Bi	15.83	0.17	0.92	12.12
114	$Sb_2(SO_4)_3$ = 0.020 g. Sb ...	15.60	0.20	1.04	11.82
115	$CuSO_4$ = 0.020 g. Cu	15.86	0.27	1.42	12.76
116	Ag_2SO_4 = 0.020 g. Ag	15.33	0.18	1.00	12.22
117	None	15.41	0.28	1.38	13.40
118	2 g. $Cr.(OH)_3$ = 1 g. Cr....	15.60	0.06	0.12	0.73
119	None	15.40	0.25	1.08	13.12

Only platinum chloride and potassium dichromate produced marked acceleration. Specimens No. 110 and No. 111 had entirely disappeared. Most of the salts, at this very low con-

centration, exhibited a slight protective action, as was noticed for silver sulphate in Test 12.

To test the permanence of the protection afforded by coatings of arsenic and tin, specimens Nos. 7, 8 and 9, of Test 3, after having stood in the air 41 days, were immersed in 10 percent sulphuric acid.

Test 16.

At 30° C. for 3 hours 35 minutes.

Specimen	Metal Coated by	Weight	Loss
7	Arsenic	16.44	0.29
8	Arsenic	16.59	0.20
9	Tin	15.90	0.20

For continued protection it is apparently necessary that some salt of the protecting metal be present in the acid.

In view of the conflicting statements in regard to the effect of the presence of copper sulphate in acid used for pickling iron, a direct comparison was made between sulphuric acid, copper sulphate and a combination of the two.

Test 17.

At 30° C. for 3 hours 35 minutes.

Specimen		Weight	Loss
120	19% H_2SO_4	15.81	2.84
121	19% H_2SO_4 + 20 g. $CuSO_4$	15.68	14.89
122	20 g. $CuSO_4$	15.55	4.22

For these particular concentrations the rate of corrosion by the mixture was twice as great as that by the two substances separately. Although the molecular concentration of the sulphuric acid in No. 120 was greater than that of the copper sulphate in No. 122, the latter proved the more active corrosive agent. In this connection it should be noted that the electromotive force of the primary cell, consisting of iron and copper in sulphuric acid, is 0.61 volts, computed from the data of Table I, while that of the iron-hydrogen cell is only 0.37 volts, minus the unknown overvoltage of hydrogen on iron in sulphuric acid. Platinum salts ought to be still more vigorous corrosive agents.

From the experiments given above, certain definite conclusions can be drawn and other generalizations now appear probable, but may require revision or rejection in the light of future experiments.

The writer's hypothesis, that the protective action of arsenic is due to its high overvoltage, has been in a general way confirmed. Other metals of high overvoltage have had a protective influence, while all metals of low overvoltage which deposit on iron are accelerators of its corrosion. So far as overvoltages are known, bismuth alone fails to conform to the hypothesis. Theoretically it should retard corrosion; actually it is an accelerator. Unless redeterminations of the overvoltage of bismuth and the single potential of iron shall reconcile theory with fact, the writer's hypothesis fails. The overvoltage of bismuth was presumably measured on a solid electrode. Bismuth deposited as a powder. If there is the same difference in overvoltage for bismuth as between smooth and spongy platinum, this correction would put bismuth in the list of accelerators.

The statements which follow are intended to apply only to the corrosion of iron by sulphuric acid.

Tin, chromium and mercury retard corrosion; of these, tin alone is as effective as arsenic. The protective action of mercury is very slight.

In studying the effect of different reagents on corrosion it is necessary to consider both the metal and the non-metal or acid radical, since each may have an effect of its own.

The binary salts and acids of the halogens are very good protective agents when used in considerable amounts. To combine most effectively the protective effects of a metal and a halogen, *e. g.*, tin and chlorine, much stannous chloride should not be added, for a large amount of the salt of any metal which precipitates on iron in an acid solution is likely to act as a corrosive agent; only a small amount of stannous chloride should be added, and the extra chlorine added as sodium chloride.

Oxidizing agents are in themselves accelerators of corrosion by acids, although in dilute solution this may be masked by a protective action which supervenes when the oxygen has been used up, as might happen with chromates.

Reducing agents should show more or less protective action, but this fact remains to be confirmed by further experiment.

In general, the whole subject as here presented is but a preliminary study which opens many possibilities for future investigation. It is hoped that the data appended may prove of service to those wishing to pursue the subject, and that the writer's conclusions may meet with confirmation from independent sources.

For convenience in comparing the effects of different reagents, an index is appended.

RETARDERS OF CORROSION

No. of Specimen

Acid, hydrobromic 109
" hydrochloric 44, 54
" hydrofluoric 98
Arsenate of sodium 7, 24, 73, 74, 75, 76
Arsenic sulphate 8
Bromide of potassium 67
Chloride of ammonium 65, 66
" " manganese 96
" " mercury 10
" " sodium 33, 48, 55
" " tin 9, 25
Chrome alum 35, 102
Chromium sulphate 17, 99, 118
Fluoride of potassium 97
Hydroquinone 62
Iodide of potassium 93, 103, 104
Mercury chloride 10
Mercury sulphate 91
Resorcine 61
Stannate of sodium 77, 78, 79, 80, 81

ACCELERATORS OF CORROSION

Acid, chromic 34, 37, 38, 39, 51
Bismuth sulphate 13, 28, 113
Chromium chloride 22, 46
Copper sulphate 3, 18, 86, 115
Gold chloride 112
Mercurous nitrate 16
Platinum chloride 89, 90, 111
Potassium chlorate 40, 107
" chromate 15, 47, 100
" dichromate 95, 110
" nitrate 36, 60, 106
" permanganate 32, 42
Silver nitrate 4, 19
" sulphate 83, 84, 85, 116

OF NO EFFECT OR DOUBTFUL

Ammonium sulphate	64
Antimony sulphate	5, 14, 31, 114
Boric acid	71
Citric acid	72
Potassium sulphate	63

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DISCUSSION.

PROF. C. F. BURGESS: Thousands of tons of acid are used annually for pickling purposes, and it is surprising that, in view of the tremendous application of these pickling processes, there has been comparatively little published on the action and the constitution of sulphuric acid itself. Dr. Watts points out that certain substances like arsenic retard the rate of corrosion. It is of especial interest to note that adding a little hydrochloric acid would not increase the rate of corrosion, but, on the contrary, it retards it very greatly. Other chlorides do the same thing. Adding salt to sulphuric acid will retard the action. There are certain other substances which will increase the activity of the acid, one of them being the bichromates, which are frequently called "inhibitors."

PRESIDENT W. R. WHITNEY: A great deal has been done in attempting to produce iron which will have less tendency to corrode. I would like to see this paper discussed at length.

DR. CARL HERING: Dr. Watts' suggested explanation, based on over-voltage, is very interesting, and seems to me plausible.

It recalls the question I asked before this Society some years ago: What is the physical meaning of this over-voltage? If, for instance, two cells for decomposing water are made exactly alike except that the cathodes are of different metals, then in sending a current through them in series exactly the same quantity of water will be decomposed in both, yet one will consume more energy than the other. The question therefore arises: What is the physical explanation of the consumption of this extra energy and what becomes of it? I presume it is safe to guess that it will appear somewhere as heat.

Another remark of interest was that the over-voltage is probably considerably less when the electrode is rough than when it is smooth. It seems, in other experiments also, that gases liberate themselves much more freely from small particles than from flat surfaces. There is an illustration of this in the typical champagne glass, with its deep tube in the stem of the glass. This tube always has some particles of dirt at the bottom because it can not be cleaned like other portions of the glass, and it is at the bottom of this that the gas always prefers to be liberated. In a really clean glass the champagne would probable appear flat, although as a fact it would really be retaining more of its gas, because that property which seems to correspond with "over-voltage" is greater.

DR. ALLERTON S. CUSHMAN (*Communicated*): Mr. Watts' paper opens up an interesting field of inquiry, although it should be pointed out that it is one in which the controlling factors are exceedingly complex and, up to the present time, but little understood.

The phenomenon of over-voltage is unquestionably but one of the factors which controls the rapidity of corrosion (or solution) of a metallic surface immersed in a more or less dilute mineral acid. But even the phenomenon of over-voltage is profoundly influenced by a number of variables. Caspari used the designation "over-voltage" to express the excess voltage required to begin the disengagement of hydrogen from a metallic surface, as compared with a platinized-platinum electrode. It has been shown that the fact as to whether or not hydrogen is absorbed by the metal to a great extent governs the over-voltage. All

metals which, like iron (steel), absorb hydrogen in large amounts have low over-voltages, and *vice versa*.[1] In addition to this, the smoothness or condition of the metallic surface is an important factor.

A piece of cold-rolled sheet steel will have a lower solubility and higher over-voltage than the same sample which is annealed without subsequent cold-rolling. Moreover, a very slight change in the chemical constitution of the steel, in respect to the number and quantity of impurities which may be present, brings in a number of additional variable factors.

We have still to find an entirely satisfactory explanation of the following anomalies, over which I have pondered from time to time for a number of years. If a specimen of sheet iron or steel is immersed in dilute sulphuric acid containing a very small quantity of arsenic, the solution of the metal is retarded. If, on the other hand, we alloy a small quantity of arsenic with iron and roll the material into sheet form, the solubility is accelerated. In the case of copper we find just the reverse to be true; a little copper dissolved in the acid will increase the solvent action of the acid on iron, but a little copper alloyed with steel will reduce the solubility in acid to a remarkable degree.

I have attempted to explain the action of alloyed copper, at least to my own satisfaction, by supposing that its presence called for a higher over-voltage, and that the immersed metal was protected by a film of un-disengaged or ionized hydrogen. If, however, we are dealing with a steel free from copper, and put copper into solution in the acid, we get the usual depolarizing effect produced by copper unequally plated out on the iron, and thus a stimulated solvent action.

The arsenic problem presents new difficulties, and while I do not take issue with Mr. Watts' conclusion that the protective effect due to arsenic in solution is occasioned by over-voltage phenomena, I am free to confess that I am considerably at sea in respect to the explanation, and am glad to take refuge with the author in the perhaps vague assertion that "arsenic is unique among metals which precipitate themselves upon iron from solution."

[1] See Mott: Over-voltage as a Factor in the Corrosion of Metals. Trans. Am. Electrochemical Society, **15**, 569 (1909).

I have sometimes surmised the possibility of catalytic phenomena being an important factor in the solution of metals in acids, and whether or not the presence of arsenic acted as an anti-catalytic or "poison," as Bredig found it to be in his classical researches on the catalytic reactions produced by colloidal solutions of metallic platinum and gold.

Mr. Watts has pointed out another curious anomaly which requires explanation, *viz.*, that whereas it is well known that solutions of chromic acid and its salts will protect samples of iron and steel from corrosion when immersed in liquids containing them, on the other hand, when we are dealing with a fairly strong acid-immersion test, the addition of chromic acid increases the corrosion effect. I have worked on problems similar to this, as have also Friend in England and Heyn and Bauer in Germany, and it has frequently been pointed out that when mixtures of inhibitors and stimulators are present at the same time in a solution, the effect produced will depend upon the special conditions of equilibrium present in the system. I first pointed this out in a paper on the "Inhibitive Value of Certain Pigments," presented before the American Society for Testing Materials, at its annual meeting in 1908. Heyn and Bauer and Friend have shown that there is a critical concentration for each substance dissolved in water, as far as corrosion phenomena are concerned. If, however, we have mixtures of materials in the solution, it is hard to predicate the results which will be obtained. The fact that Mr. Watts has found that chromic acid stimulates corrosion under the conditions of his experiments in nowise interferes with the value of the observations that chromic acid and its salts act as strong inhibitors of corrosion under neutral as well as under very slightly acid and alkaline conditions, provided the concentration of the chromic acid ions is sufficiently great.

I have found Mr. Watts' paper an extremely interesting one, suggestive in many ways, and it is, in my opinion, a valuable contribution to studies of corrosion.

Mr. E. B. Spear: In regard to the rusting of iron in the presence of potassium dichromate, we have devised an experiment in our laboratory to show that the rate of corrosion is a function of the concentrations of the oxidizing agent and of the

hydrogen ion. Iron becomes passive in concentrated solutions of dichromate containing little free acid, while it corrodes much faster in very dilute solutions of the oxidizing agent than it does in water containing the same amount of acid. As the acid is increased, however, the concentrated solutions of the dichromate attack the iron very rapidly.

Mr. Walter A. Patrick: In order to study the effect of the concentration of the sulphuric acid, the following experiment was carried out. Two pieces of steel were secured, one of which had a high oxygen content (*i. e.*, was a poor steel), while the other was normal steel, but contained about 0.2 percent copper. Both were mild steels. Carefully cleaned pieces of these two steels were then placed in solutions of sulphuric acid, the concentration of which varied from about 25 percent down to 1 percent. In the strong acid the poor steel dissolved about 50 times as fast as the steel containing the small amount of copper, but in the more dilute acid solutions the difference between the two steels became less and less until in a 1 percent acid the poor steel was dissolving only 3 times as fast as the other steel. If the acid corrosion test were carried out upon the above samples with 20 percent acid, it would show that the copper steel was 50 times as good as the other steel; but with 1 percent acid the relation between the two steels would be only 3 instead of 50, which is probably much nearer the true value for practical purposes.

Mr. Watts (*Communicated*): Experiments in the corrosion of alloys of iron and arsenic, carried out in the chemical engineering laboratories of the University of Wisconsin, gave results opposite to those cited by Dr. Cushman. The samples containing arsenic were somewhat more resistant both to atmospheric oxidation and to corrosion by dilute sulphuric acid than the original iron. The maximum amount of arsenic in any of the alloys tested at the University of Wisconsin was 4 percent. The different results obtained by Dr. Cushman may have been due to the use of higher percentages of arsenic. But little information has been published concerning the constitution of the arsenic-iron alloys, so that it is impossible at present to predict their behavior throughout the whole series toward a corrosive agent such as

sulphuric acid. Definite compounds of iron and arsenic appear to be present in some of the alloys.

Stead[1] says: "Arsenic and iron most readily combine to form arsenide of iron. * * * We find that on solution of arsenical steel in dilute hydrochloric or sulphuric acid practically the whole of the arsenic remains as a black, insoluble arsenide of iron."

This indicates that iron is the anode in the voltaic cell formed by the contact of iron with its arsenide in sulphuric acid, and the considerable electromotive force of this cell may be responsible for an increase in the rate of corrosion of the iron when such compounds are present.

Since this alloyed arsenic is not dissolved by the acid, it fails to exert the well-known protective action produced when a little arsenic has been previously dissolved in the acid.

The iron-copper alloys, up to a content of 8 percent copper, consist of solid solutions of copper in iron.[2] They are homogeneous, and any differences in the rates of attack of such alloys by sulphuric acid, as compared with the rate at which the acid attacks pure iron, must depend upon the inherent nature of the two materials. In binary alloys which are solid solutions we would naturally expect a mean between the properties of the elements of which the alloy is composed. Copper is attacked only slowly by sulphuric acid. It is therefore to be expected that alloys which consist of solid solutions of copper in iron will resist corrosion by sulphuric acid better than iron. This proves to be the case.

[1] J. Iron and Steel Inst. 1888, I, 180.
[2] J. E. Stead. J. Iron and Steel Inst. 1901, II, 112.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

AN ELECTROLYTIC METHOD FOR THE REDUCTION OF BLUE POWDER.

By Warren F. Bleecker.

The substance commonly known as blue powder is a usual by-product of almost all, if not all, processes of zinc smelting. It occurs in the ordinary zinc condensers in quantities varying from two or three percent up to twenty percent of the zinc condensed as spelter, depending particularly upon the type of condenser, but also upon many other factors of the smelting process used.

Blue powder is essentially metallic zinc in a very finely divided condition, each particle coated with a film of microscopic thinness, and this film is the direct cause of the powder remaining as such, even at a temperature far above the melting point of zinc. I have never determined the chemical composition of this film, nor have I ever seen published a conclusive analysis. It is generally concluded that the greater part of the film may consist of zinc oxide, but there are known to be present traces of elements other than oxygen. Since blue powder does not occur in a pure state, but is always contaminated with other substances introduced mechanically with the zinc fume, a satisfactory examination would be very difficult. In these experiments it is unimportant whether the film consists wholly of oxide or not, since the quantity is so small that the amounts of energy involved are practically negligible.

Blue powder obtained by me from various sources contained from 80 percent to 95 percent zinc, the higher grade, however, representing what is known as refined zinc dust.

While there is a market for a limited amount of some of the grades of blue powder, there exists the practical problem of reducing to spelter any excess of this quantity which may have been produced during the smelting and condensing processes. It was an attempt to solve this problem that led to the results and

data given here. The work is unfinished, but the results as they stand may be of interest, and serve to illustrate the application of electrolysis to problems of this character.

For convenient reference, some of the physical data upon which the experiments were based are here noted, and their application will be apparent. For the sake of simplicity, and because of disagreement, only approximate values are set down.

	Melting Point.	Boiling Point.
Zinc	420°	920°
Zinc chloride	262°	730°
Sodium chloride	820°	
Sodium sulphate	863°	
Zinc fluoride	734°	
Sodium hydroxide	300°	
Sodium zincate	above 800°	

Sodium-zinc chloride melts between 600° and 800°, depending upon the amount of zinc chloride and sodium chloride present.

After experimenting with a considerable number of compounds which might possibly be used as an electrolyte, zinc chloride was found to give by far the best results.

It will be seen that this compound is almost ideal in consideration of the conditions existing. It melts and becomes fluid at a temperature of more than one hundred degrees below the melting point of zinc, even below the temperature of ignition of zinc dust. Zinc chloride does not begin to vaporize until the temperature has risen at least three hundred degrees above the temperature at which zinc becomes fluid enough to settle out of the bath. It is non-corrosive to iron containers, and doubtless to other materials with which it might be desirable to construct furnaces. The specific gravity is less than molten zinc, thus allowing the spelter to settle to the bottom of the furnace. It is a relatively cheap substance, and I shall finally suggest a possible source of zinc chloride from which it may be obtained for practically nothing and in an unlimited supply.

A double chloride of sodium and zinc was tried, but the melting point of the bath was so high that there was serious loss of zinc by volatilization, and in addition the recovery was low and the current consumption high.

Likewise sodium zincate melts at too high a temperature to be of use in the operation of this process. The zinc separates

beautifully from a fused caustic soda electrolyte, but as soon as the reaction between the electrolyte and the mechanically mixed zinc has been completed (after fifteen minutes or less), the bath becomes sticky and the melting point rises to such an extent that the zinc begins to fume and the blue powder to ignite when added.

Sodium zinc fluoride, zinc fluoride, zinc sulphate, zinc nitrate, and a number of other substances were tried, but without success. Reference to the melting points of most substances otherwise suitable will suggest that they are not adapted to satisfactory use in this particular process, although other conditions than those under which I worked might yield better results with some of these materials.

The operation of reducing the blue powder was carried on in an iron pot which I had designed for another purpose. This pot was hemispherical, and had two lugs extending outward from the top. It was about nine inches across the top on the inside and six inches deep, the thickness of the iron being a little over half an inch throughout. The lugs served to support the pot as well as to afford a means of cool connection with the conductor from the generator. It was supported by a brick furnace which could be heated with gas.

An excellent connection between the iron lug and the copper terminal was made by introducing a sheet of silver between the cleansed surfaces and bolting the two firmly together. Obviously the pot served as the cathode element in the process.

The anode consisted of a rectangular piece of Acheson graphite made of three strips 12 x 12 x 0.5 inches (30 x 30 x 1.3 cm.) bolted together. It was supported by a heavy block of iron, into which was screwed an 18-in. (45 cm.) length of ¾-in. (2 cm.) gas pipe at right angles. The pipe ended in a tee, the long portion of which had the threads removed so that it could slip up and down over an upright pipe bolted to the floor by means of a sidewalk flange. This arrangement permitted the electrode to hang perpendicular and to be readily moved up and down for regulation of current density, and also to swing clear of the furnace when desired.

The current was furnished from a Bogue 6-volt, 1,200-ampere generator of standard type, which could be arranged to give a

voltage of 15-20 volts by connecting the two commutators in series.

In beginning a run the zinc chloride (previously dehydrated) was introduced into the pot and melted by the heat from the gas burner. This operation required but a short time and the fused chloride became a quiet, thin fluid which showed no tendency to vaporize unless heated excessively. Naturally, before we learned to control the operations, the bath was often overheated with a resulting loss of zinc chloride and a very unpleasant atmosphere.

The introduction of the anode caused some difficulty at first, because of the cooling effect upon the bath immediately surrounding it. The electrode conducted the heat away so fast that it maintained a solid coating which would not conduct the electric current. The difficulty was overcome by the obvious device of preheating the electrode with the flame of the burner to a temperature somewhat greater than that of the bath.

With the furnace in readiness as described, the current was started, with a difference of potential between the electrodes of 15 volts. This was not necessary, but was done in most cases to insure a rapid starting in case the pot should be oxidized inside, or a high resistance encountered at some other point. As soon as the low reading ammeter showed 50 amperes, or thereabouts, the commutators were connected again in parallel.

The blue powder was added to the bath about a pound at a time, and either stirred into the bath with a stick until thoroughly mixed, or covered with the fluid by splashing. If the powder were not soon covered it would catch fire and burn on the surface, not only resulting in a loss of the powder itself, but also in overheating the electrolyte at the edges of the burning powder, with a further and personal discomfort.

Upon adding the powder a moderate evolution of gas occurred, which burned at the surface with a continued series of minute explosions. The flame of the burning gas was bluish, similar to that of carbon monoxide. This evolution continued for not more than a minute after each addition of powder and can be accounted for by assuming that the film covering the zinc particles consists of material other than oxides or carbonates, possibly carbide. It would be a very simple matter to obtain a

quantity of this gas for analysis, and the results would be worth while, for information could be thus gained as to the composition of the film.

As the blue powder is mixed into the electrolyte the chemical reaction between the zinc chloride and the film of the zinc particles seems to take place very rapidly, the mass becoming entirely homogeneous and remaining quite fluid. If more than half a pound of blue powder per pound of electrolyte be added, the bath tends to thicken, and the action of the furnace is retarded, although not stopped. After a few minutes the bath becomes thin again and no damage has been done unless too much heat was applied in order to attempt to obtain the proper fluidity by heat alone.

The spelter begins to deposit at once and accumulates rapidly in the bottom of the pot. The quantity of gas evolved at the anode is smaller than might be expected. At times there appears to be also a slight evolution of gas at the cathode.

An examination of a cooled portion of the electrolyte soon after the addition of the blue powder shows the presence of the zinc in a finely divided condition, but bright and free from coating. Some of the phenomena of separation from this point on appear to be mechanical, since some spelter will deposit upon continued heating without the passage of the electric current. Just why the passage of the electric current should so greatly increase the rate of separation, as well as the quantity separated, is not altogether clear, since it is evident from the powder consumption that but little if any of the zinc is dissolved. The particles are so small, however, that they tend to remain in suspension, even though the electrolyte be as fluid as water.

With everything going smoothly the voltage is maintained at about five and the amperage between one hundred and two hundred, depending upon the interval between additions of the powder. At above two hundred amperes the bath becomes overheated. By regulating the anode density we succeeded in maintaining the required temperature reasonably well, but as a matter of safety we usually kept the current just low enough to permit of the pot being heated with gas at intervals of five or ten minutes.

The blue powder was added at intervals somewhat irregular,

but averaging about two minutes. The greatest amount of blue powder treated during one run was 25 pounds. The reason for not making a longer run was twofold: Our supply of blue powder was always limited, and we had no means of tapping the pot, but had to remove the spelter by first dipping out the electrolyte and lastly the zinc itself.

The power consumption during the several runs was fairly uniform, and averaged one-tenth kilowatt-hour per pound of spelter recovered. Considering the quantity of material to be electrolyzed, this is excessive, but taking into account the quantity of material under treatment, specific heat, physical condition, and radiation losses in such a small apparatus, it is indeed hopeful. Further than this, it may be reasonably expected that in a larger furnace the consumption would be much less.

The recovery was in all cases very high, usually greater than 100 percent, due to the constant electrolysis of the electrolyte. We never reached the limit to which a bath could be used, although there is a continued loss of zinc chloride from several causes, such as, volatilization because of overheating, reduction by electrolysis, formation of salts such as chloride of iron, silicate of zinc, etc., mechanical losses.

After the electrolyte becomes fouled with impurities to such an extent that it can be no longer used, the zinc chloride remaining in it may be recovered by leaching with water acidulated with hydrochloric acid. If not too much acid be used, the resulting chloride will be quite pure enough and will contain but a trace of iron. The process of dehydrating the zinc chloride is not difficult nor is it unusually expensive.

The grade of spelter recovered bears a reasonably constant ratio to the grade of the raw material, since the process is evidently not one of refining. From blue powder containing zinc 83 percent, iron 0.98 percent, lead 2.1 percent, the spelter ran zinc 91 percent, iron 1.75 percent, lead 3.5 percent. Another sample of blue powder with zinc 81 percent, iron 0.71 percent, lead 0.53 percent, yielded a spelter which assayed zinc 95.1 percent, iron 2.5 percent, lead 0.8 percent. One lot of refined zinc dust assaying 92 percent zinc yielded a spelter of over 96 percent grade.

These results are not entirely conclusive as to grade,

because in several instances impurities were knowingly added. For example, the iron in the runs mentioned above came in part from the apparatus and tools used. Since there were no arrangements made for tapping off the spelter, a quantity of the electrolyte was dipped into the mould with the spelter in spite of all precautions, and the cooling took place so rapidly that some of this, at least, remained mechanically mixed with the zinc.

I may add that one attempt was made to tap off the spelter by drilling into the bottom of the pot and running a small iron pipe to the outside of the furnace wall. This pipe was closed by an iron cock. Just as the pot was ready for the first tapping, the pipe split along the weld and the entire melt was lost. Some scraps of spelter which were later recovered by tearing the furnace apart, notwithstanding the presence of much dirt and admixed oxide, ran above 95 percent zinc.

Naturally one cannot draw correct conclusions when the evidence is not all at hand, but from the results actually obtained we should be justified in making the following statements:

Unquestionably, blue powder can be transformed into spelter without the use of reducing agents, such as carbon, and at a temperature not far above the melting point of zinc.

There appears to be very little corrosion of the graphite anode, and no sloughing of the alloy formed on the inner surface of the cathode.

The operation would seem easily to lend itself to a continuous process; in fact it looks as though the process must be continuous in order that the best results may be obtained. In a continuous operation on a large scale it is difficult to see how the proportion of impurities in the spelter can be greater than in the blue powder, assuming that no impurities are derived from the electrolyte.

If a low grade of blue powder is treated, the spelter will be of low grade, and if there is no market for this product, the process is useless from a commercial standpoint.

In the production of spelter of equal grade, the process is far more efficient than reduction by carbon, from the standpoint of energy and manipulation.

If a blue powder of sufficiently high grade can be made by any process of electric zinc smelting, so that a commercial grade of

spelter can finally be produced, the entire cost of zinc smelting ought to be materially reduced, and the combined processes be less complex and unsatisfactory than those now in use. In other words, if the blue powder problem were the chief problem in electric zinc smelting, then this reduction process, properly developed, should afford a satisfactory solution.

It is entirely possible that the condenser itself could be made into a furnace for the reduction of blue powder by lining it with a cathode material, and in this way avoid heat losses and additional handling of materials. In this case the problem of feeding would be eliminated, although this should not prove serious in any event, since the powder could easily be fed through a hopper which would introduce it under the surface of the electrolyte.

Although the loss of zinc chloride appears to be small, say one pound per twenty-five pounds of spelter recovered, yet the loss cannot be overlooked. And while zinc chloride may be obtained cheaply as a by-product from processes other than zinc smelting, it seems possible that certain products containing zinc which are now worse than wasted might well be used for the source of the electrolyte. In the concentration and separation of zinc-lead-iron sulphide ores there are four products, namely zinc concentrates, lead concentrates, an iron product, and silicious tailings. These three latter products carry more or less zinc values, depending upon the nature of the ore treated and the milling process. These three products might be made to give up a large portion of their zinc content by a process of dry chlorination at a very low cost. It has been demonstrated that if zinc sulphide is ground to extreme fineness and treated with warm chlorine gas, the sulphide is acted upon with the formation of zinc chloride, which may be extracted by leaching with water. The reaction is exothermic, as may be seen by inspecting the heats of formation. The molecular heat of formation of zinc sulphide is about 45,000 calories, and that of zinc chloride is about 97,200 calories. If the temperature is properly controlled, the lead and iron sulphides ought not to be attacked to any great extent, and if attacked could be rendered insoluble.

If zinc chloride could be cheaply made in this manner on a large scale, as laboratory experiments indicate, there would be the additional advantage of saving zinc otherwise lost, and refin-

ing to a degree other products which are usually penalized because of their zinc content. The reduction of the zinc obtained in this manner would cost nothing, since the charge would stand against the blue powder reduction.

The production of zinc chloride by roasting low grade ores with salt would not be satisfactory because of the presence of sodium salts and other undesirable impurities all of which would have to be removed before the product could be used as an electrolyte in this process.

Mr. Arnold J. Guerber and Mr. J. Ross Corbin were of great assistance to me in the theoretical and practical work as described.

DISCUSSION.

Mr. Alfred Sang (*Communicated*): The results secured by Mr. Bleecker are of great interest even tho the spelter obtained was so hard that its commercial uses would be limited.

The main point of interest would be to examine what advantages may be secured by substituting electrolytic reduction for redistillation. The old Montefiore system required 550 kgs. of coal to recover 700 kgs. of zinc;[1] it was abandoned because the zinc was too high in iron and because, with careful handling, better economy could be secured by redistillation; a lower percentage is recovered, but less coal is consumed.[2] Redistillation of dust alone will give a metal containing 0.7 percent of iron;[3] Mr. Bleecker's percentage is much higher and equivalent to the iron content of the original dust.

The value of zinc chlorid as a flux for hot galvanizing is well known, and when a bath is so high in aluminium that it no longer oxidizes at the surface and sal ammoniac finds nothing to "feed on," it is used to great advantage. I have found that it readily permits the sherardizing of aluminium, the adherence of the zinc being perfect. The only way to get a thin coating of flux is to dip the article in it when at a temperature higher than that of the fused chlorid.

[1] Kerl's Metallurgie, transl. Crookes & Rohrig (1869), **1**, 453.
[2] Massart, Rev. Univ. des Mines, **30**, 201.
[3] Jensch. Zeits. d. Oberschles, Bergh, u. Hüttenb. Ver., **29**, 355 (1890).

With regard to the evolution of gas, the greater part of this gas is undoubtedly hydrogen. Moisture and cold water are decomposed slowly, and hot water rapidly, by zinc dust, and the absorption of hydrogen may amount to 50 times the volume of the dust.[4] When fresh zinc dust is heated for the first time it gives off a great deal of gas the odor of which is unpleasant; until all the gas is baked out any sherardizing performed with it has a very poor appearance.

The action of the current in aiding the precipitation of the zinc in a metallic form is undoubtedly related to the peculiarly unstable condition of amorphous zinc dust, evidenced by many phenomena, such as the absorption of heat on cooling,[5] its crystallization at low temperatures when under high pressure,[6] and Cowper-Coles' observation that an electrolyte having zinc dust in suspension deposits more than the theoretical weight of zinc. Mr. Bleecker was working with ideal conditions at the cathode and with zinc dust in suspension in his electrolyte.

Dr. Carl Hering: The process is also interesting in that it seems to be a case in which the suspended material is affected by the current while it is between the electrodes, that is, when not in contact with the electrode, otherwise the blue powder would be reduced by simply heating it in molten zinc chloride, and Mr. Bleecker says that without current it does not go down as zinc. It reminded me of some experiments which I described in a paper to this Society some years ago. In these I found, under the microscope, that small particles which were suspended in the electrolyte traveled with the current; it therefore occurred to me that this might explain why these little particles of melted zinc, suspended in the liquid, are carried down to the anode. The ampere hour efficiency being more than 100 percent in this test described by Mr. Bleecker shows that some of the zinc must be carried down otherwise than electrolytically.

Mr. E. B. Spear: I want to call attention to the statement in one of the discussions read on this paper: "Electrolytic zinc usually contains zinc oxide on the electrode." I have called attention to this in an article entitled "Causes for High Results in

[4] G. Williams, Chem. News., **52**.
[5] Sang, Trans. Am. Electrochem. Soc., **20**, 259 (1911).
[6] W. Spring, Rap. Congr. Intl. Phys., **1**, 412 (1900).

Electrolytic Determination of Zinc," in the American Chemical Journal, **32**, 533.

MR. WARREN F. BLEECKER: It is more or less unimportant, but this is not a patented process and probably never will be; it is simply presented as a scientific fact, and if anyone can make any use of it he is welcome to it. I make this statement in order that the process may be used and developed in any way and put to commercial use; I shall be glad to see it done by anyone who may be interested.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18 1912, President W. R. Whitney in the Chair.

HIGH TENSION EQUIPMENT FOR ELECTROCHEMICAL PLANTS

By J. Rattray Wilson.

The design and equipment of the electrical end of a modern electro-chemical or an electro-metallurgical plant is of endless detail, and calls for a very careful consideration of the process to which it is to be applied. With regard to the high tension part, however, this is now practically standard, and it is to this part that the author devotes this paper.

The difference between the modern power station and the average manufacturing plant is that in the power station the employees are all more or less experienced men, while in the factory anybody seems good enough—men who do a little of everything and are none too good at the best. In many cases they do not even have a working knowledge of the English language, and the foreman's knowledge of the language of gesticulation being equally deficient, the latter does not seem to understand the difference betwen the lack of understanding and deafness.

With this end in view the installation must be of the most simple construction, as nearly "fool-proof" as it is possible to make it, and also easily accessible should repairs or alterations have to be made. There is one rule which ought always to be enforced, and this is that no unauthorized person ought to be allowed in the high tension department. Secondly, all operating devices on the low tension side must be so placed that the employees can get at them without leaving their places. Thirdly, all dead metal exposed, such as switchboard frames, switch levers, transformer cases, generator and motor frames, etc., and, if possible, one pole of the secondary circuit, ought to be thoroughly well grounded, the ground wire of ample capacity, and arranged so that it may be very easily inspected. The author knows of more than one case where attention to this detail has been the means of avoiding a lot of damage.

In the vicinity of Niagara Falls the primary current is delivered at a tension of 11,000 and 12,000 volts, and until recently it was all brought to the consumer's premises on overhead cables. On the American side this overhead construction is largely being done away with, the conduit system taking its place. This alteration saves a great deal of trouble, as it eliminates to a very large extent the heavy surging from lightning or other external causes. It is more expensive to construct, but no doubt it will pay in the end; it also saves unsightly poles, thus tending to the better appearance of the town.

In bringing in the overhead power cables the author has made it a rule to have these about 20 feet (6 m.) above the

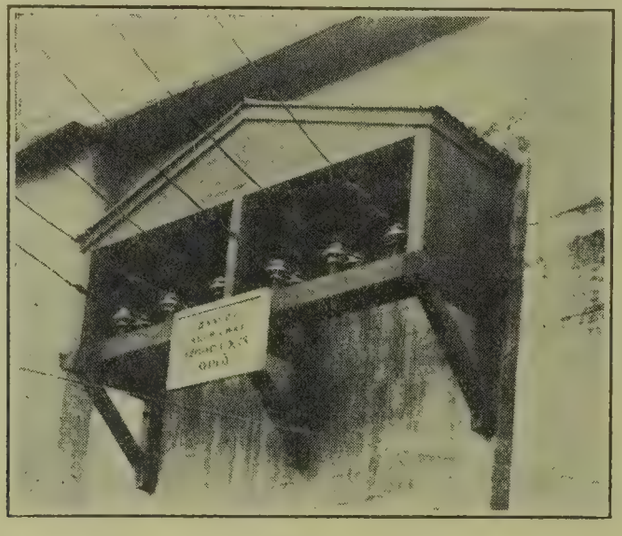


FIG. 1.

ground, 18 feet (5.4 m.) being a minimum. This allows plenty of clearance for wagons, as the pole line generally follows the roadway, or there may be crossings that cannot be avoided. The cables are brought to terminal insulators fixed to the wall; as a rule the power company's jurisdiction ends at this point, they making the connection to the consumer's station here.

The author prefers to build a special intake tower for this purpose, containing all the incoming switches, lightning arresters, main circuit breakers and necessary meters. This tower can be located where convenient, but it ought to be as central as possible, and where extensions are contemplated, these have to be taken into account when making the designs. From this point the various circuits are run to the different buildings.

The terminal insulators of the transmission line are fixed to

the wall at the height before mentioned, or the conduits, if these are used, brought through the base. The overhead wires or cables are brought into the tower through porcelain tubes of proper insulating resistance. Both the terminal insulators and the leading-in tubes are protected from the weather by some kind of hood, that designed by the Ontario Power Co. being as serviceable as any (Fig. 1). Immediately on the inside of the wall the cables are connected to the disconnecting switches, each conductor having its own switch. In polyphase installations where more than one set of incoming cables are required, each

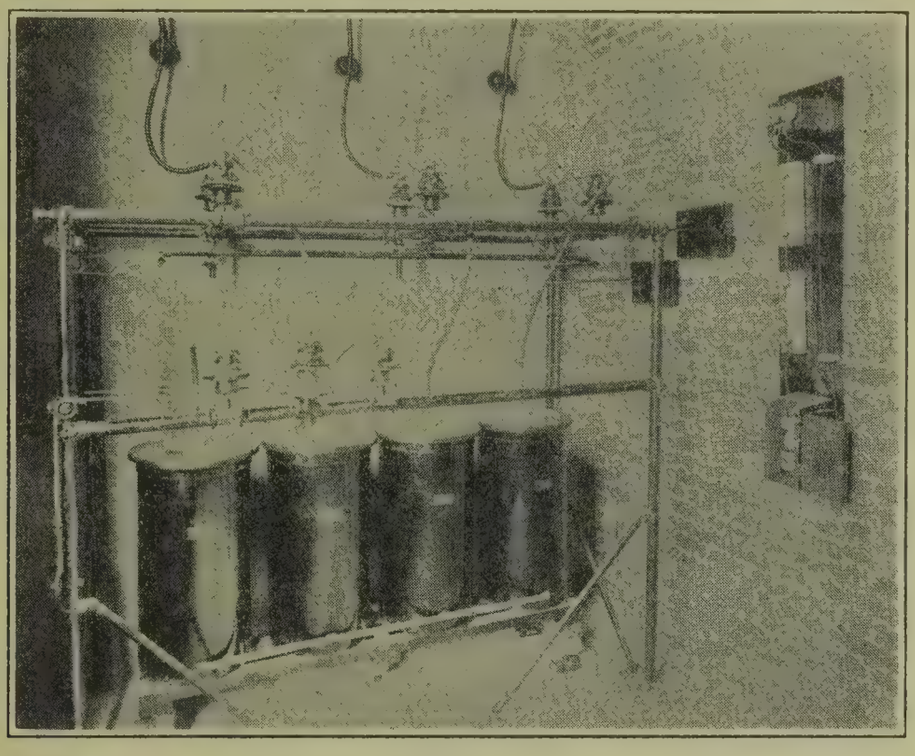


FIG. 2.

phase is connected, on the consumer's side of the disconnecting switches, to its own "busbar." This allows any line to be cut out when required. It is generally well to provide space at this point for more than one set of power lines. These switches must be of ample carrying capacity and clearance, and are operated by an insulated hook. Needless to say they must never be operated unless the main circuit breaker is open. They may be installed either with or without insulating barriers, according to the space at disposal.

Immediately below the disconnecting switches the connections for the lightning arresters are made, and conductors run to the

arresters. These ought to be located in a place by themselves, a part of the tower being bricked off for them (Fig. 2), the electrolytic type at present being the most used. The rope for swinging the horn-gaps is led outside this chamber, thus giving the operator an element of safety which is desirable, for, especially during the time of electrical storms, the best of arresters are not to be trusted. All arresters ought to have their own disconnecting switches, in addition to the horn-gaps. With this arrangement the whole apparatus can be cut out for repairs.

Returning to the main conductors, these are led through properly designed choke-coils, to flatten out any surging of the current, and from there to the main oil circuit-breaker. This oil-breaker must be a heavy one, and if the factory is close to the power station, as they are in Niagara Falls, the best is none too good. The author once heard it solemnly stated that "circuit breakers were unnecessary in a well-designed furnace plant." This may indeed be the case where the source of energy is in the factory itself, and the engine, or other prime mover, is of the same capacity as the generator. The capacity of the latter being just equal to the load, the effect of a surge would be to slow down the whole installation, or to stop it altogether in the case of a short-circuit in the furnace itself, a condition that may easily happen.

Few factory engineers (and this also applies to electrical contractors) seem to recognize the fact that this circuit-breaker may have to open the whole power-house load, plus any surges that may be on the line at the time, and the power-house engineer, knowing this, ought never to connect up to a consumer without seeing that everything is well protected. This condition, unfortunately, is not always observed.

In or around Niagara Falls, on all installations over 1,000 k. w., a hand operated circuit-breaker, type "H-4," of the General Electric Co., The Electrical Conduit Co's type "F" or type "FH," or a Westinghouse type "C," is recommended; under that capacity a breaker equal to the Westinghouse type "E" is the smallest that should be used. In some instances even a larger breaker might be advisable. At first sight this may seem excessive, but the factory engineer has no means of knowing whether his line is connected to one unit, or to the whole power-house,

or, for that matter, to two or three power houses, all interconnected in order to help one another out.

For factory purposes breakers are usually hand operated, as the extra expense of the additional apparatus required to operate the electrically operated type as a rule is out of the question, to say nothing of the extra complications and care.

This main breaker can be placed where convenient; in the case of the General Electric Co's type "H-4" the author mounts this on a platform, as it is bottom connected. With this type the tripping relays are so arranged that they are operated by the high-tension current, thus saving the cost of series transformers. (See illustration in Mr. A. J. Jones' paper, published in the Transactions of this Society, **20**, 488.)

Immediately behind this breaker the power company's instruments are located, as well as any other high tension instruments that may be required; this arrangement makes a neat installation, as all the incoming apparatus is in one place. From this room the various circuits are run wherever required. All cables are taken through walls in porcelain tubes, and the writer makes it a rule that no high tension conductor, or any other part of the high tension circuit, shall be nearer the floor than 7½ ft. (2.25 m.) unless absolutely unavoidable. The cables or conductors are best supported on pipe-brackets carrying the necessary insulators, and are tapped for the various transformers or motor generators, as the case may be, each transformer having its own set of disconnecting switches and oil circuit-breakers. The taps are first brought to the disconnecting switches, then to the series transformers operating the trip coils, then through the oil circuit-breakers to the transformers or motor generators, as the case may be (see Fig. 3).

These circuit-breakers are mounted on pipe framework, and are kept as high as circumstances permit, the operating mechanism being led outside the high tension room, and placed where convenient. It would be a great improvement on these smaller circuit-breakers to have the tripping mechanism mounted on the switch itself, as is done in the larger sizes. This would obviate the placing of glass protection boxes around the remote control. The tripping mechanism being usually placed there, is liable to be disarranged by grit and chemical fumes; at the same time it

is liable to be tampered with, it being often easier to alter the trip than to find the trouble on the circuit.

At this point it may be interesting to state that between the disconnecting switches and the transformers a water rheostat is

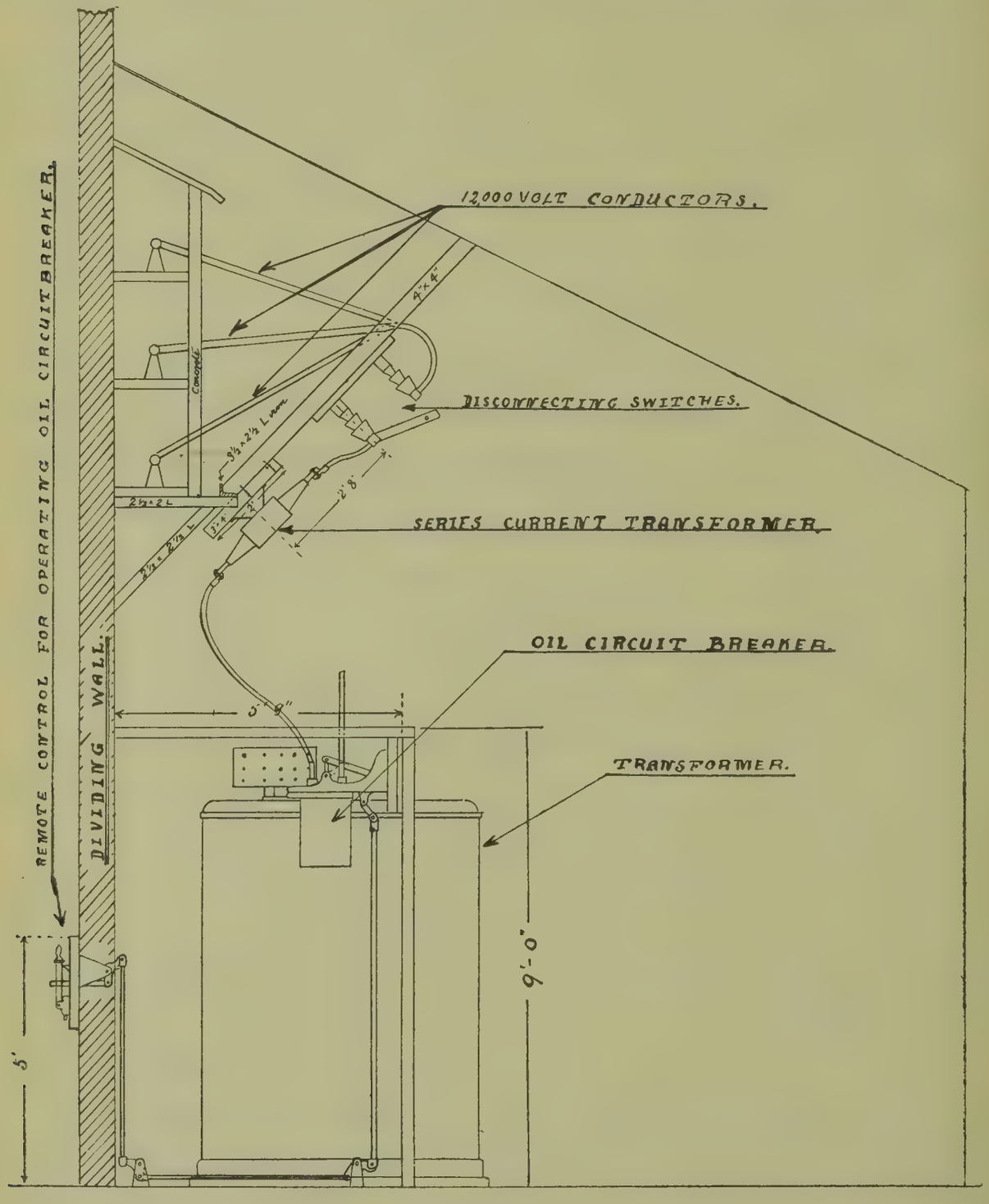


FIG. 3.

sometimes placed; a special, single pole, oil circuit-breaker being used to short-circuit it (Fig. 4). Where transformers have to be started under full load, this rheostat is of much greater importance than it would seem. In the first place, it is impossible to

determine which phase the transformer circuit was opened on, and consequently when starting it may be closed on a reversal of magnetism, thus causing a dead-short-circuit, so to speak. Secondly, when closing-in on, or near, the top of a wave, surging is sure to follow, and it is no uncommon thing to find the circuit-breaker coming out four or five times in succession; thirdly, closing a transformer circuit under full load will cause severe stresses in any case. The transformer builders recognize this, and now

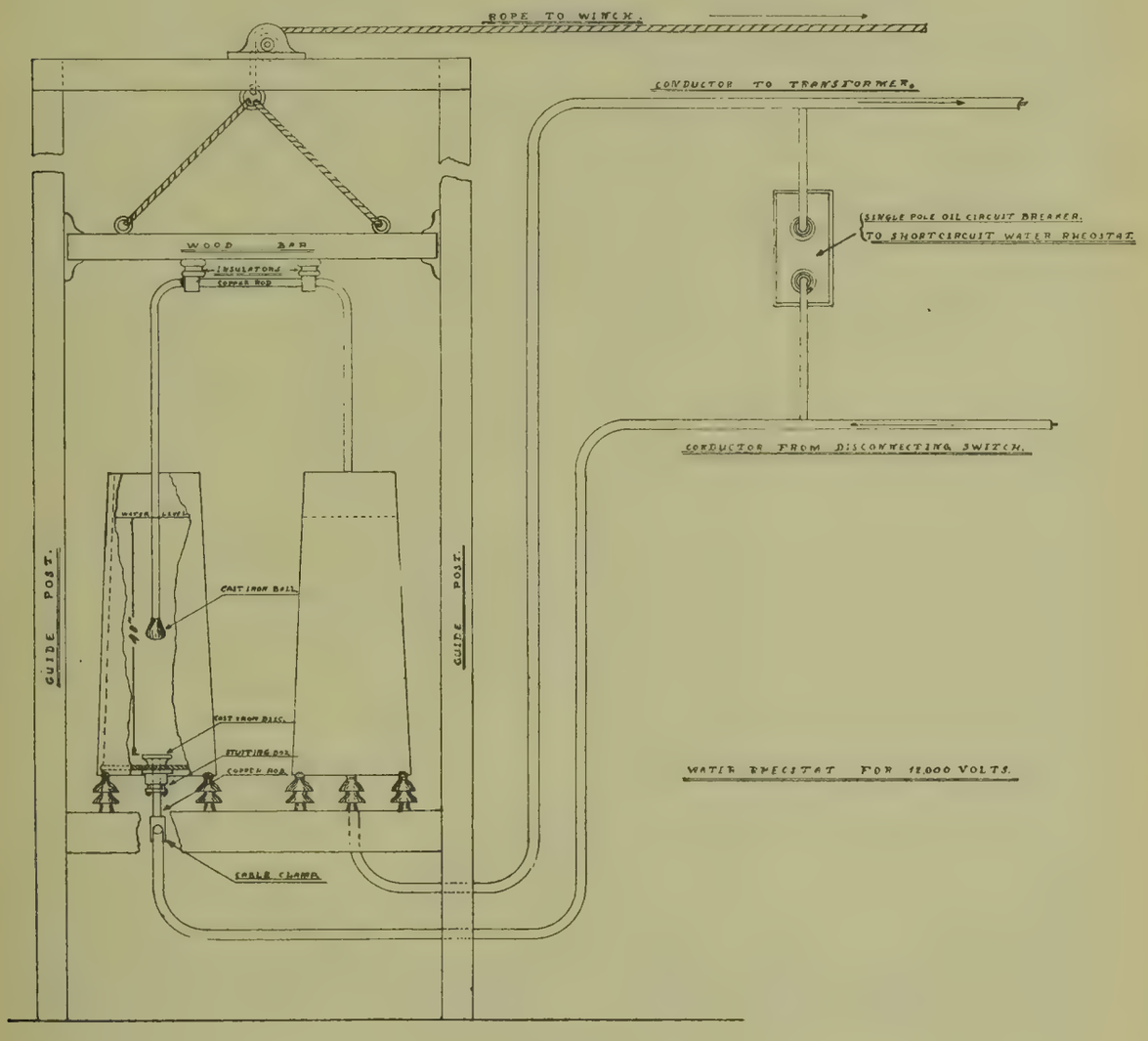


FIG. 4.

build choke-coils in the case, along with the other parts. Although this helps to a large extent, it is not adequate in all cases.

The effect of a long column of water acting as a resistance allows the transformer to pull into step, as it were, without undue stress. In starting a 750 k. w. transformer, with 12,000 volts on the primary, under the most severe working conditions the author could devise, the immediate starting current never exceeded one-sixth of the normal working current. The construction of this

rheostat is very simple. Two wooden tanks are made and set up on petticoat insulators, supported on either a wood or a pipe frame. A loop from one of the poles is cut, one end brought through the bottom of one tank, and the other through the bottom of the other. These cables terminate in cast-iron discs. The closing mechanism is a copper rod of suitable cross-section, fixed to but insulated from a wood bar, the wood bar being capable of being raised or lowered, and kept in position by sliding in grooves. To the ends of the copper rod are fixed cast-iron balls to give surface for the current to pass to or from the water, also to act as contact or arcing pieces, in conjunction with the metal discs mentioned above. Both the discs and the balls are screwed onto copper rods so as to be easily replaced if necessary, the rods to the discs passing through stuffing boxes on the under side of the tanks. The movable rod is bent "U" shaped so that the vertical portions are coincident with the vertical axes of the tanks. This rod is raised or lowered by a rope, leading through pulleys to a winch placed in a convenient position in the low-tension room.

The method of operation is as follows: The oil circuit-breaker is closed on one pole, the copper rod is next lowered slowly till it makes contact, then the short-circuiting switch is closed, thus closing the other pole; the rod is then raised to the top of its run ready for another occasion. The rheostat may be used for breaking circuit provided the column of water is long enough, but it is very much better practice to use the oil circuit-breaker, which is designed for this purpose, as the stress which may be set up by the change of frequency due to the arc being maintained on the top of the water may cause troubles of its own. The writer believes that this rheostat was first developed by the Niagara Falls Power Co., for use on its 2,200-volt circuit, where the charging currents must of necessity be heavy; since then it has been modified to conform to varied conditions.

In arranging a bank of transformers on a three-phase circuit for single-phase work, it is as well to equip every fourth unit with two single-pole, double-throw, disconnecting switches. These switches are so wired that the transformer can be thrown on any phase, so that when a furnace is down for repairs, the circuit may be kept in balance. At times this may be of some assistance

to the power house, if their load gets out of balance, as any phase may be loaded to suit them—a little courtesy which they appreciate at times.

In furnace work especially, owing to the very heavy currents employed in the secondary circuit, it is good practice to get the transformers as near to their work as possible, so that the transformer room must be located with this end in view. In designing a new plant this can very easily be arranged by keeping the transformer room parallel to the furnace room, merely separating the two by a brick or concrete wall, the electrical apparatus being on one side and the furnaces on the other. This room is roofed over complete in itself. By this means it is possible to keep the electrical plant reasonably free from dust; many troubles can be traced to inattention to this simple arrangement.

Interlacing of the low-tension conductor bars, watchfulness in seeing that all exposed non-conducting metal is well grounded, and, in the case of reinforced concrete dividing walls, paying attention to the placing of the reinforcing steel so that there can be no closed magnetic circuits, all tend to a sucessful installation.

The author is indebted to the various power companies and electrochemical engineers in Niagara Falls for their kindly co-operation.

DISCUSSION.

Mr. J. L. Harper (*Communicated*): The subject of high-tension wiring in connection with modern electrochemical and electrometallurgical plants is one of vital importance to the central station operators, and especially at Niagara Falls. Here the greatest plants of this nature in the world are concentrated, requiring continuous 365-day-per-year power, and in many cases even a temporary but complete interruption causes the customer extended loss far beyond that proportionate to the length of the shut-down.

Knowing the requirement of their own processes, power-users are inclined to desire to so arrange their own receiving station and wiring that it shall reduce the possibility of circuit-breaker

openings or other interruptions to a minimum, thus throwing back upon the generating system all the troubles of which they can possibly get rid.

This requires the central station designers and operators to make preparation for a varied and continuous attack of troubles coming in over their lines from so-called "fool-proof" and "screwed-down" factory installations, causing many times varied and unexpected surges and fluctuations not only in their voltage and current curves, but also in sudden unbalanced or low power-factor conditions, the power-user often not caring whether the power is obtained three-phase or single-phase, so long as his furnace is kept at running heat. It was originally considered good design, and the indication of laudable caution, to install lightning arresters or surge protectors to protect the wiring and generating system from injury, both in the case of the overhead line and the underground conduit distibution, but within the past few years, when plants, especially at Niagara Falls, have grown to such proportion that there are often 50,000 to 100,000 horse-power connected into one system, it is noted that the old spark-gap system of lightning arresters generally operate on one surge or discharge, then are cut out for the reconstruction of that part of the building in which they were located. The more recent development of the electrolytic lightning arresters has also shown that one discharge is often sufficient to require the purchase of an entirely new set of aluminum hats, and much explaining is necessary to convince the owners of the generating station and the customers of the necessity of the shut-down. Therefore, central station men are becoming more interested in the factory wiring, for the reason that under most conditions it is found that the whole system may now be designed to withstand any surges or fluctuations that are set up from any source, and as these, with the exception of lightning, come principally from trouble in the factory, it is apparent that that part of the system should be given special care.

In the case of a short circuit in which, say, 50,000 horse-power in generating capacity is connected to the system, the energy to be interrupted attains gigantic proportions, as, under short-circuit conditions, the generators momentarily give out power said to be from five to twenty times the rated capacity of the machines,—

this factor, however, depending upon the "fly-wheel effect" or energy stored in the rotating parts of the machinery. Therefore, it has become necessary to produce switches not only for the central station, but also for the receiving station at the power-user's end of the line, that will be of the proper capacity to interrupt the circuit without regard to the specific amount of power being used by the customer, but dependent rather upon the maximum capacity of the generating station. Switches of this nature are now being developed by the large manufacturing companies, and in a recent extended line of experiments new forms were tried out by the writer for interrupting the power from four 10,000 horse-power units operating in synchronism, the complete interruption being accomplished in approximately one-third of a second and without detrimental effect either to the switch or to the system.

Another, and often unsuspected, cause of trouble is the surge thrown into a system at the time of the "cutting-in" of large motors or banks of transformers without the proper protective devices; also, operators of large central stations are now beginning to suspect that even the frequent charging and discharging of the electrolytic lightning arresters has caused very high frequency fluctuations in their lines which may be responsible for the otherwise unexplained burning-out of the coils in their alternators or high-potential motors which are nearest to the power leads. Therefore, at the present time it is believed to represent good judgment, in all except long overhead lines, to consider most protective devices as causing more trouble than they are worth, to make a study of the factory ends of the distributing lines in order to produce a minimum of fluctuations, surges or unbalancing conditions, and to develop and use, both in the central station and at the receiving end of the lines, switches having a capacity commensurate with the whole capacity of the generating plant back of them.

Mr. Philip P. Barton (*Communicated*): I have read the advance copy of this paper, and I think the author may desire to correct a statement which appears at the top of page 372. The statement to which I refer is as follows:

"In the vicinity of Niagara Falls the primary current is

delivered at a tension of 11,000 and 12,000 volts, and *until recently it was all brought to the consumers' premises on overhead cables. On the American side this overhead construction is largely being done away with, the conduit system taking its place.*"

This statement hardly does justice to the Niagara Falls Power Company, which, in 1895 and 1896, delivered power by means of underground cables to its earliest electrochemical customers, the Pittsburgh Reduction Company and The Carborundum Company. So far as my present recollection serves me, it has never delivered power to any electrochemical customer by overhead circuits, but from the beginning has served such industries by means of underground construction, in which it did a great deal of pioneer work.

MR. J. RATTRAY WILSON (*Communicated*): I am very glad to hear Mr. Harper speak from the position of the generating station engineer, and his reference to the effect of the kinetic energy of the rotor is interesting. The subject of lightning or surge protectors is a point that is wide open to discussion, and as Mr. Harper says, whether they are necessary or not, is greatly dependent on the location of the consumers' factory with regard to that of the power house. I note that Mr. Harper calls attention to a "fool-proof" and "screwed-down" installation. I should say that an installation that can be "screwed-down" is either "fool-designed" or "fool-operated," and it is just this point that should be strictly attended to. A consumer or his engineer must on no occasion throw his troubles on either the power house or his neighbors; in fact, he must remember that he is but a unit in the whole.

I am greatly obliged to Mr. Barton for pointing out this omission. The Niagara Falls Power Company adopted the conduit form of distribution from the very first.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

POWER SUPPLY TO ELECTRIC FURNACES FOR REFINING IRON AND STEEL.

By W. Sykes.

Up to the present time, comparatively little attention has been paid to the question of the power supply to electric furnaces, more thought having been given to the characteristics of the various types and constructions from a metallurgical standpoint. This is only natural, as it was to be expected that in the early stages of development, the design of the furnace itself would be considered more important than the influence of the various characteristics upon the power supply.

It has been generally assumed that very cheap power is necessary to insure economical operation of electric furnaces, but this is not necessarily the case, as an excessive electrode consumption or excessive wear of linings may easily offset a considerable difference in the cost of power.

An examination of some of the results obtained in Europe in the production of electric steel from the product of the Bessemer converter shows that in the case of arc furnaces, at least, the cost of power is not by any means a controlling feature. It is of course desirable that the power consumption and cost should be reduced to a minimum, but it is erroneous to assume that an electric furnace cannot be economically used unless very cheap power is available.

The individual characteristics of the different types of furnaces influence to some extent the power costs, and these features will be considered later.

At the present time I think it is safe to state that within a comparatively few years the electric furnace will have supplanted the crucible for the production of fine grades of steel, as there is no doubt that the cost of producing such steels is very much less with the electric furnace as at present built than in the

crucible. On account of the large quantity of metal that the electric furnace can handle, it presents considerable advantages for certain industries when producing high grade steel. An instance of this is the production of large ingots for gun barrels, such as are made at the Krupp Works. Before the introduction of the electric furnace these ingots were made by pouring an enormous number of crucibles into the mould. Now, three or four electric furnaces are used and the labor of several hundred workmen is dispensed with.

It is my opinion, however, that the great field of the electric furnace is in the production of such steel as is used for structural

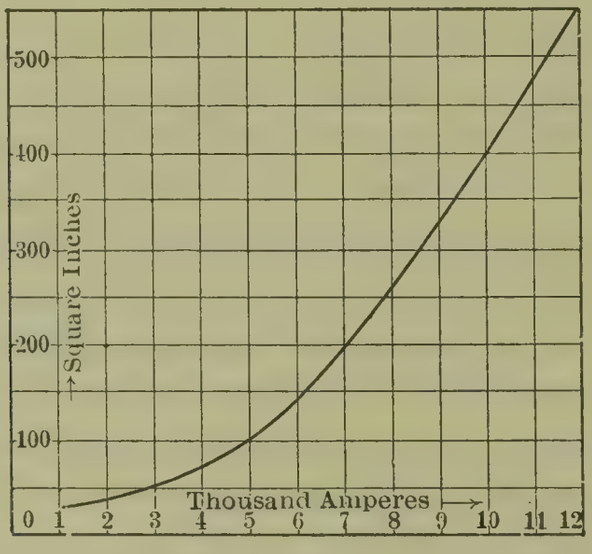


FIG. 1.—Electrode Sections for Arc Furnaces.

purposes. During the last few years there has been an increasing demand for special grades of rails, structural shapes, etc., and this demand has been more or less satisfied by using special qualities of open-hearth steel, but every year the specifications are becoming more and more stringent and the difficulty of insuring good results is increased. It is in this field that the electric furnace, in my opinion, has its greatest scope.

Before it can be entirely successful, it will undoubtedly be necessary to modify certain features in the construction so as to allow of using larger furnaces than are now met with. The question as to the type of furnace that will eventually survive is one for the future, but I do not believe that we will find any one type of furnace supplanting all others, as undoubtedly the different constructions have certain fields of application for which they are most suited.

Generally we are concerned with the two principal types, the arc and the induction furnaces.

Arc Furnaces: At the present time, arc furnaces of the Heroult type with a capacity of 15 tons are in operation, these furnaces using 3-phase current with three electrodes. The current handled is about 12,000 amperes and it is necessary to use electrodes approximately in 24 in. (60 cm.) in diameter. The difficulty of constructing such large electrodes makes it improbable that very much larger currents will be handled by a single electrode, especially when it is remembered that the current density must be decreased as the size increases.

In Fig. 1 is shown the size of electrode that has been used in a number of installations for different sizes of furnaces and it

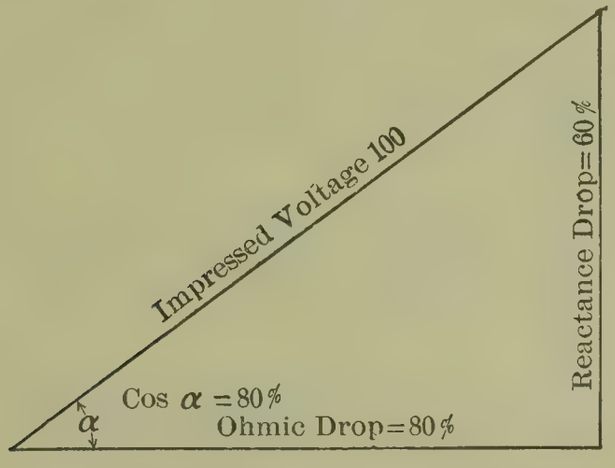


FIG. 2.—Diagram for 15-ton Arc Furnace.

will be seen that the dimensions of the electrodes increase very rapidly when the current exceeds about 6,000 amperes. It is probable that in designing furnaces of say 30 to 50 tons capacity two or more sets of electrodes will be adopted, as single electrodes over about 600 sq. in. (3,750 sq. cm.) in section are not likely to be used. This will complicate to some extent the construction of the furnace, and considerable development will be undoubtedly necessary to satisfactorily handle the numerous electrodes.

A furnace with six electrodes has already been built and is in operation, and it is therefore clear that without any very great difficulty we can increase the size of the furnaces from 15 to 30 tons by simply duplicating the electrical equipment. Further development along these lines is problematical on account of complications, but it is a question whether furnaces larger than

about 30 tons are necessary or desirable. The handling of currents even of 12,000 amperes presents considerable difficulty, not only from the standpoint of conduction, but also on account of the effect of the self-induction of the leads on the power factor of the equipment. In a 15-ton furnace with about 12,000 amperes per electrode, the power factor is approximately 80 percent. This condition is shown in Figure 2, from which it will be seen that the reactance voltage is 60 percent of the impressed voltage. With a fixed frequency and voltage, this furnace is taking almost the maximum amount of power that can be put into it.

In the diagram the hypothenuse represents the impressed voltage, the horizontal the ohmic drop and the vertical the reactance drop which is at right angle to the ohmic drop. The effect of these factors on the power input to the furnace has been discussed by Mr. K. C. Randall in a paper read before this society in May, 1910. Below is given some of the conclusions arrived at in this paper and the influence of the self-induction is clearly demonstrated.

1. The maximum power in a system containing reactance occurs when the total ohmic voltage equals 71 percent of the impressed voltage.

2. The maximum power occurs in a furnace with resistance load when the power factor of the system is:

$$0.71\sqrt{1+\frac{R}{\sqrt{p^2L^2+R^2}}}$$

when R and L are respectively the resistance and self-induction in the circuit.

3. The input to a given circuit for a given frequency is proportional to the square of the impressed voltage.

4. The maximum energy that can be fed into a constant voltage circuit at different frequencies will be inversely proportional to the frequencies, and will exist at a power factor of 71 percent.

From the above it is obvious that the reactance must be limited as much as possible, and an examination of existing furnaces shows that considerable trouble has been taken by interlacing the conductors to reduce the self induction. It is probable, however,

that before handling larger currents some structural changes will be necessary to avoid running the conductors close to iron supports, etc., and also to reduce their length.

The variation of load in a furnace of the arc type has some effect upon the power station, but the reactance of the furnace is generally sufficient to limit the current to such a value that no particular damage is done by short circuits. The short-circuit current of the usual arc furnaces on 25 cycles is generally about twice the normal current. On referring to Fig. 2, it will be seen that when running at 80 percent power factor the short circuit would be:

$$\frac{\textit{Impressed Volts}}{\textit{Reactance}} = \frac{100}{60} = 1.66,$$

or somewhat less than twice the normal operating current. When a large number of furnaces are used at one plant, the effect of the variations in current during operation would not be very great, and it is only when considering small installations that particular attention need be given to this feature.

In the case of a single furnace, provision must be made in the power house to take care of short circuits in the furnace, since they are unavoidable. The frequency of these short circuits is dependent upon the regulating mechanism of the furnaces, which is one of the details that must be given more attention in the future than in the past.

Induction Furnaces: The induction furnace has several advantages over the arc furnace, which make it of considerable importance not only from a metallurgical standpoint, but also from the standpoint of economy. The fact that the heat is generated in the metal to be refined and that it can be regulated very accurately is of considerable importance, especially when producing fine grades of steel, as it eliminates the liability of local overheating, which is possible with an arc which normally has a temperature of about 3,500° C., making it necessary to always interpose a slag between the electrode and the metal. The great advantage of this type, however, is the elimination of the costly electrodes and connections.

There are certain limitations, however, as to the sizes in which these furnaces can be built, which no doubt will be overcome in

the future, as they are connected more or less with the electrical design.

At the present time, the pure induction furnace, of which the Kjellin is typical, is rather in disfavor on account of the poor power factor at ordinary frequencies, especially in the larger sizes, and to improve conditions very low frequencies have been adopted in a number of cases. Fig. 3 shows what has been done in this respect in Europe, and indicates the extremes to which the designers have gone in order to compensate for this characteristic of the furnace.

The introduction of the Röchling-Rodenhauser furnace has considerably improved the operating characteristics of the induc-

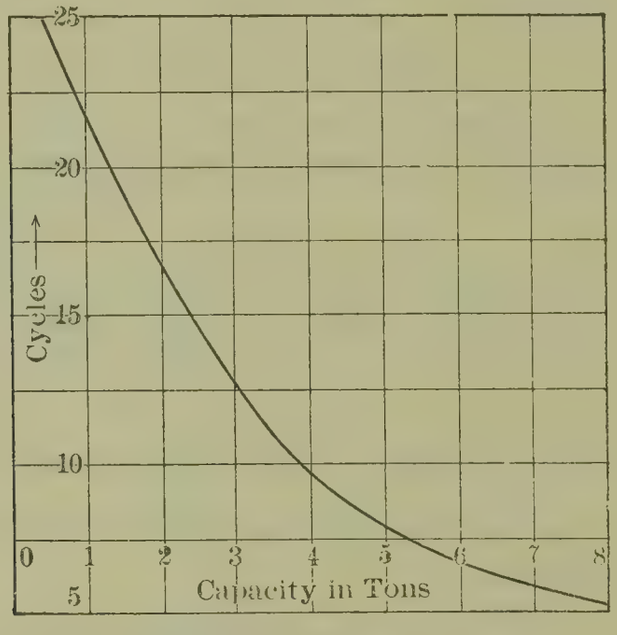


FIG. 3.—Kjellin Furnaces Installed.

tion furnace by combining it with the resistance type and by properly proportioning the dimensions of the furnace and the ratio of the power absorbed as a resistance furnace to the total. Reasonable power factors are thus obtainable even with comparatively large furnaces and commercial frequencies. The effect of a low power factor on an ordinary station is to appreciably reduce the capacity of the plant, as it is seldom that the generators are designed for a power factor of less than 80 per-cent, and in most of our steel mills synchronous motor-generator sets are used to improve the operating characteristics of the plant by compensating the low power factor of the induction machines.

When considering a new station for the operation of induction furnaces, it would undoubtedly be cheaper to install generators with a large kilo-volt-ampere (K.V.A.) capacity compared with the size of the prime movers. The cheapest way to take care of the wattless component is undoubtedly to increase the size of the generators. If the generating plant is already installed, it is necessary to provide other means for accomplishing the same purpose, and in general two methods are available; one is to use

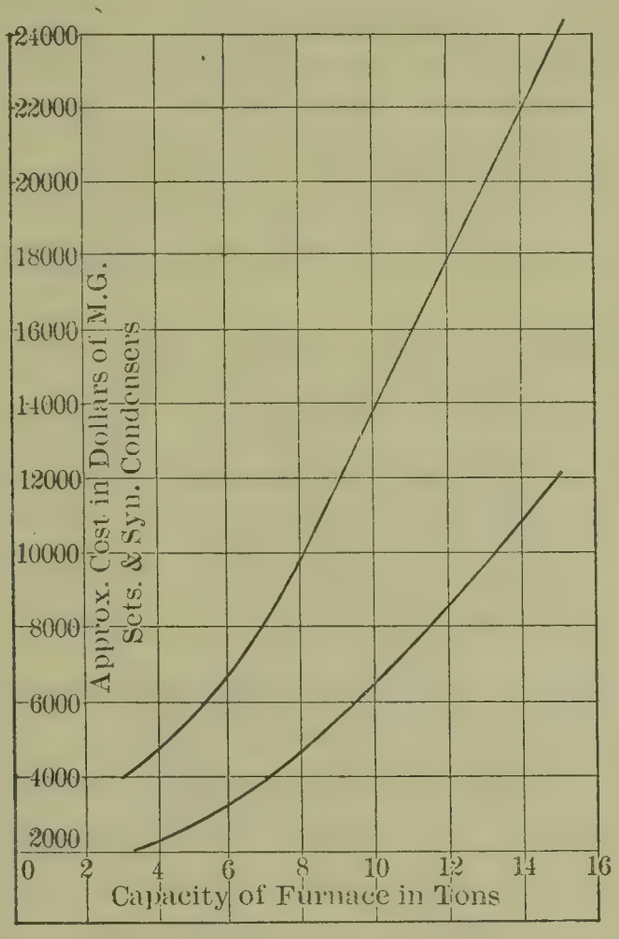


FIG. 4.
Upper Curve—Motor Generator Sets.
Lower Curve—Synchronous Condensers.

a motor generator set either with a low-frequency generator, or one of large K.-V.-A. capacity, and the other to use a synchronous condenser which will compensate for the low power-factor of the furnace.

When using a motor-generator set, the regulation can be taken care of by varying the excitation of the generator. In such cases, where the furnace is connected directly to the line it may be found necessary to use a transformer in order to give lower voltage on the furnace and also for the sake of regulation. The

usual voltage in large plants is 6,600 volts and the frequency 25 cycles, but there is no particular reason why this cannot be taken care of in the design of the transformer in the furnace, so that we have in one case a motor-generator set for the full capacity of the furnace and in the other a single synchronous machine with capacity equal to the wattless component only.

The difference in cost of such arrangements is shown in Fig. 4, which shows the relative costs of synchrouous motor-generator sets and a synchronous condenser for various sizes of Röchling-Rodenhauser furnaces for 25 cycles; both arrangements giving unity power on the line. In addition to the saving in the first cost of the synchronous condenser, there is also a saving of approximately 6 to 7 percent of the power required for the furnace, owing to the smaller losses compared with the motor-generator set.

From these curves it is obvious that when furnaces are installed on existing power stations and trouble is caused by low power-factor, the proper arrangement is to install a synchronous condenser instead of a motor-generator set. In the case of frequencies higher than 25 cycles this also holds good, although with 60 cycles the saving is somewhat less.

Resistance Furnace: The use of resistance furnaces for the refining of iron has been limited to very small sizes, on account of the difficulty of handling the very large current necessary. At various times resistance furnaces have been proposed, but owing to the structural difficulties they have not been successful. In order to obtain a conductor of considerable length the surface exposed is necessarily great, and this is not conducive to economical operation. The limitations of the resistance furnace may be best illustrated by an example of how such a furnace would have to be constructed. Assume a furnace of 10,000 pounds (4,550 kg.) capacity the bath having a section 12 x 4 in. (30 x 10 cm.) the length would be:

$$\frac{10000}{0.283 \times 12 \times 4} = 735 \text{ inches. (18.5 meters.)}$$

The specific resistance of the iron at the usual temperature of the furnace, about 1,600° C.-1,700° C., is not very certain, depend-

ing upon the composition, etc. A good average figure based on a large number of tests is,

0.0000665 ohms per cubic inch.

The resistance of the above furnace would be therefore,

$$\frac{735 \times 0.0000665}{48} = 0.00101745 \text{ ohms.}$$

Normally a furnace of this size would absorb about 600 kw. and the current should be therefore,

$$\sqrt{\frac{600{,}000}{0.00101745}} = 24300 \text{ amperes,}$$

and the voltage

$$24300 \times 0.00101745 = 24.75 \text{ volts.}$$

The above calculation is based on using direct current. In the case of alternating current the conditions are somewhat more favorable, but the above is sufficient to show that this construction is not practicable in large sizes. In the construction of electric furnaces it is necessary to reduce the area of the surface of the molten metal as much as possible in order to limit the conduction and radiation losses, and such a furnace as outlined above would be very poor in this respect on account of the great area exposed, and consequently the power consumption would be very high.

Electric Pig-Iron Furnaces: It is incorrect to refer to the electric furnace used for the production of pig iron as a blast furnace, but the latest development in this type of furnace in Norway has shown in reality that we are developing electric furnaces capable of replacing the blast furnace in making pig iron.

In this case, the problem of introducing power to the furnace is not very different from that of the arc refining furnace, but it is a great deal easier to arrange the electrodes so as not to interfere with the operation of the furnace, as no tilting arrangements are required. In general, it may be said that the economy of such furnaces will be increased as the power concentrated

in the furnace is increased. The use of such furnaces, however, is necessarily limited to a few localities where fuel cost is high and power is cheap.

By careful design and operation, however, the type of furnace has been brought to the stage where it may now be considered commercial. The latest published results show a power consumption of 1,736 kw. hours per ton, which at $8.00 per h.-p. year is equivalent to $2.10 per ton for power. The consumption of charcoal is 740 pounds costing $2.25 and the electrode consumption has been reduced to 12 pounds per ton of pig iron, costing approximately $0.50, so that the total cost of power, charcoal and electrodes is now about $5.00 per ton of pig iron produced. It will be seen that under these conditions the electric furnace can be used commercially for the production of certain grades of pig iron where conditions are favorable.

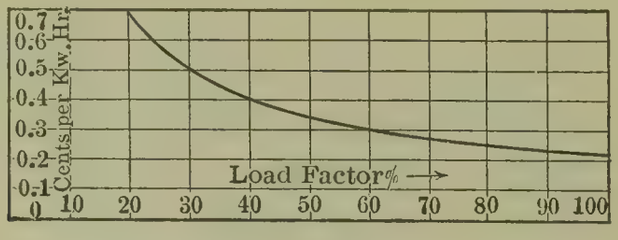


FIG. 5.—25,000 kw. Station; 5,000 to 6,000 kw. Sets. Coal, $1.25 per Ton. Capital, $50 per kw. Installed.

Power Generation: Undoubtedly, the cheapest method of generating power is to use water-wheel-driven generators, when the development of the water power does not involve a very great capital outlay. The cost of power in some localities has been reduced to very low figures on account of the small development required for the installation. For instance, in Norway, power is generated at a cost of from $4.00 to $8.00 per h.-p. year. Where the initial development is expensive and transmission lines are long, it is not always most economical to use water power, especially if cheap fuel is available close to the location where the power is to be used.

As an illustration of the possibility of producing power from coal cheaply, the curve in Fig. 5 shows the estimated cost of power generation with a steam plant under favorable conditions. This curve is based upon actual operating figures and may be taken as being representative of what may be obtained. The

capital cost of the station has been taken at $50.00 per kw., and the fuel cost at $1.25 per ton. The size of the station has been taken at 30,000 kw. installed, which would be suficient for the refining of a maximum of 1,000,000 tons of Bessemer steel per year, producing a steel of somewhat better quality than that now furnished by the open-hearth furnace. Assuming the maximum output to be 3,000 tons per day and that 10 heats would be obtained from each furnace, the total operating capacity would be 300 tons. Assuming 10 furnaces of 30 tons, it is probable that the maximum number operating at full capacity would not average more than eight. With an input of 3,000 kw. per furnace the maximum load would be in the neighborhood of 24,000 kw. leaving 6,000 kw. to spare. Allowing for business fluctuations, the output per year would not be more than about 700,000 tons. With a power consumption of 150 kw.-hours per ton, the load factor will be 50 percent. The cost of power per ton of steel will be:

$$150 \times 0.0034 = \$0.51 \text{ per ton.}$$

With an electrode consumption of six pounds (2.7 kg.) per ton, the cost of electrodes will be $0.35. From the above it is obvious that the cost of power is not by any means always the controlling feature, and there is no reason why mills in localities where fuel is cheap should not install electric furnaces.

Other sources of power are available that are at present neglected. A considerable portion of our blast furnace gas is still wasted, but in modern mills there would not be any surplus available for generating power for furnaces if the mills are electrically driven, and it is probable that the extra power requirements would have to be supplied from a steam plant.

In the Connellsville Coke district there is produced yearly about 18,000,000 tons of coke, the gas being wasted. If this gas were collected there would be continuously available, besides the by-products, about 250,000 kw. if burned under boilers or 500,000 kw. if used in gas engines. Whether under the existing conditions in Pittsburgh it would pay to use this gas, in view of the cheap fuel, is problematical, but it is a field that may be developed in the future.

From the figures given above it is clear that the cost of power

is by no means the principal item in the expense of electrically refining steel, and that quite as much, if not more, can be accomplished in the reduction in the cost of production by reducing the consumption of electrodes, linings, etc., as by reducing the power cost.

DISCUSSION.

HENRY D. HIBBARD (*Communicated*): The chapter of this paper on "Power Generation" contains a somewhat fanciful foray into the future, and its justification is doubtful. The cost of plant is not given in detail, but in no place that I know of can a cost of steam-power station of $50 per kw. be met if every actual item of cost be included, even on such a great plant as one of 30,000 kw. capacity. In estimates of cost of such plants necessary items are often omitted, such as some or all of the cost of land, grading, railroad tracks, water supply, cranes, coal-handling plant, ash-handling plant, interest during erection, general expense during erection, legal expenses, and damages to employees or others. Then, any given site is likely to demand extraordinary items or extraordinary increase of some items. A trestle, piling or other excessive provision for foundations, a wharf, or unusual length of connecting track, may be needed.

The cost of good fuel of $1.25 per ton is only attainable at points very near to coal mines. The resulting cost of power given, about one-third of a cent per kw. hour, is probably unattainable in any steam-driven plant now or in the future.

The cost of electrodes, though outside the subject of the paper, is considered, but the figures are perhaps even less entitled to escape criticism. The cost of electrodes, estimated at 25 cents per ton of steel, is but a small fraction of the actual costs so far achieved; they range usually from 6 to 10 times that figure, with occasional costs of from two to four times that, taking in each case a cost per month as the unit.

MR. SYKES (*Communicated*): From Mr. Hibbard's discussion it is evident that he is not familiar with the conditions existing in our steel plants. Information furnished me by a number of

plants in the Pittsburgh district shows that the cost of their generating plants, including everything in connection with them, works out to an average somewhat less than $50 per kw. installed.

Steel plants must be necessarily favorably located, otherwise they cannot compete, and generally conditions are such as to make possible the installation of cheap generating stations.

The items enumerated by Mr. Hibbard, such as cost of land, grading, railway tracks and water supply, are seldom of great importance, because steel works are always located favorably with regard to such items. The other items are only the general expense incurred in the building of the power plant.

Regarding the cost of fuel, it was pointed out in my paper that these figures referred to a plant favorably located. It is safe to state that there is not a steel plant in Pittsburgh paying as high as $1.25 per ton for coal. The average cost of coal delivered at the plant is usually about $1.00 per ton. Regarding the cost of power, this is mainly a matter of load factor, and there is at least one steam plant in the Pittsburgh district that is generating power at a lower figure than given in my paper. This plant is paying $1.06 per ton for coal. Another plant using blast furnace gas and working with a load factor of 55 percent is producing power at a cost of 0.35 cent per kw. hour. In this case the gas is charged for on the basis of calorific power at the same rate as if coal were used. This cost includes all overhead charges.

Regarding cost of electrodes, Mr. Hibbard is apparently not familiar with the latest results that have been obtained with electric furnaces. Using sectional electrodes it is quite possible to obtain an average consumption, when refining steel under the conditions mentioned in the paper, of 6 pounds per ton. Such electrodes cost approximately 5½ to 6 cents per pound. These figures have been obtained with Héroult furnaces, and are the average of several months' operation. The figures given by Mr. Hibbard are altogether abnormal, and show that either the electrodes are of poor quality, that they are too small, or that the furnace is improperly operated.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

FURNACE ELECTRODES PRACTICALLY CONSIDERED.

By R. Turnbull.

A number of papers have been read at the various meetings of this Society during the last two or three years, and articles published in the technical papers, on electrode losses, but, so far as I am aware, the practical end of the electrode question has never been taken up by any one of our members except in a very superficial manner.

It therefore occurred to me that as electric furnace practice is only confined to a very small percentage of the members of this Society, and as there must be quite a number who have never encountered electrode troubles, and who may not understand what benefit the Society is getting from the above mentioned discussion on electrode losses, that for these reasons a practical paper written on the subject of electrodes by one who has been in the business for a number of years might prove of some benefit to the members as a whole.

Before going into the history of the electrode, let us first see what relation it has to the electric furnace. Putting it in its simplest form, the electrode is to the electric furnace what the steam pipe is to the steam engine. In the latter case the steam or source of energy is carried to the engine in the pipe at a certain pressure, represented by pounds per square inch and the volume of steam by the number of cubic feet. To get more power, should the volume be increased the pipe must be made larger in diameter, in order to avoid frictional losses, etc. The same result could be attained, within a certain limit, by increasing the pressure and allowing the volume to remain the same. In the case of the electrode, the pressure and volume of the steam are replaced by volts and amperes; an electrode, if large enough, will carry to the furnace a certain number of amperes with very little loss in volts, but as the amperes increase, the section of the electrode must also be increased, otherwise the loss in volts by

resistance in the electrode will become serious and considerably decrease the output of the furnace. As in the case of the steam pipe, the pressure in volts might be increased in order to get more power into the furnace, but electric furnace operation is generally controlled by the voltage, and a variation from the usual number of volts would upset the good operation of the furnace.

Now let us examine what an electrode is composed of, and what constitutes a good and a bad electrode.[1] The mixture used in the manufacture of the ordinary electrode is anything but a complicated one, being simply some kind of carbon mixed with certain percentages of pitch and tar. This, after being well mixed together, is moulded in some special apparatus to the desired form, and then baked in a furnace in a non-oxidizing atmosphere. This looks simple, and when one looks back on the troubles and tribulations experienced by technical men in electric furnace work over quite a number of years, due mainly to bad electrodes, it seems strange that the secret of making electrodes which would not break was not discovered long ago. But good electrodes were made from the very beginning, and it is quite possible that amongst the first batch of electrodes made some were equal in quality to the best electrodes made at the present day. This was where the great difficulty confronting the manufacturer lay, in his ability to, unintentionally, turn out a first-class electrode and a thoroughly bad one at the same time and under exactly the same conditions. Electrodes made at the same time, under the same conditions, and baked in the same furnace, have shown in actual service as many different characteristics in quality as could well be imagined, some giving excellent service whilst others simply went to pieces after being in operation for a few minutes.

As the electrode is to the electric furnace what the gasoline motor is to the aeroplane, one can well imagine what a bad electrode meant to the operator of the electric furnace; without the efficient gasoline engine the aeroplane would probably be unknown, and the same might be said would be the case of the electric furnace without good electrodes.

[1] There are two classes of electrodes, the amorphous carbon and the graphite; it is the former to which I wish to draw attention, as graphite is prohibitive for ordinary furnace practice, owing to its high cost.

In the early stages of electrode manufacture petroleum coke was mostly employed, it being first of all calcined to drive off all volatile matter. This was afterwards replaced by retort carbon, a kind of coke which is deposited in the retorts in gas works, and which is nearly pure carbon. Better results were obtained by the use of retort carbon than with petroleum coke, and it was considered for a time the only material with which a reasonably good electrode could be turned out. I have not sufficient data to enable me to say when and where the first large electrodes were made, but I should not be far wrong in saying that they were first made by Dr. P. Héroult at his works in Froges, France, some fifteen years ago; at that time he made then as large as 16 inches (40 cm.) square and 6 feet (1.8 m.) long. Some of these first electrodes manufactured by him were very good, and some very bad, and little if any reliable data could be collected from his work. I should like to say here, however, that Dr. Héroult has not abandoned the field, he having established works in Niagara Falls, N. Y., where excellent electrodes are now being turned out, and although the process used is different in some respects from his original one, he is still working along the same lines. His original process is still being used with good results at Welland, Ontario, by Electro-Metals, Limited.

Now, what was the reason of so many failures to turn out a good article in the early days, and why do nearly all electrode manufacturers, even those who have been but a short time in the business, turn out today a fairly satisfactory article? I think I am not far wrong in saying that the main cause of failure was in the use of the wrong carbon material. Petroleum coke did not work well, and electrodes made from it crumbled to pieces in the furnaces. Retort carbon made a better electrode, but as this commodity was collected from gas works all over the world, a homogeneous article could not be counted upon, and this made its use dangerous to the manufacturer, so far as reliability was concerned. It was only when anthracite coal came into use that real progress was made, and the best kind of electrodes in use today are made from this material. Hardmuth, of Venisseux, France, was, if I am not mistaken, the first to use anthracite coal on a large scale, and for some time his electrodes

were the best in the market. He was quickly followed by the German makers, the Plania Werke and Siemens. We are indebted today to the Plania Werke for the moulded screw, which enables electrodes to be joined together, thus doing away with the stub and machining of the electrode and the trouble of changing electrodes in the furnace. This screwed electrode applies mainly to furnaces for the manufacture and refining of steel. At the present time nearly all manufacturers are using anthracite coal as the carbon base, and while electrodes made by some manufacturers are superior to those made by others, this is mainly due to the different methods of moulding the electrodes and preparing the coal employed.

So much progress has been made in this industry in the last two or three years that perfectly satisfactory electrodes up to 24 inches (60 cm.) in diameter and 7 feet (2.1 m.) long are now being made, whilst only a few years ago nothing over 12 inches (30 cm.) square and five feet (1.5 m.) long was satisfactory. No doubt still larger electrodes can and will be built, as electric furnaces are still growing in size, and the time is not far distant when steel furnaces of 30 tons' capacity, and operating with electrodes three feet (0.9 m.) in diameter, will be as common as are our small 5-ton furnaces of today.

Before closing this paper, I would like to give a few hints as to the best manner of employing an electrode in order to ensure the best service and avoid the losses of which we have heard so much. Carbon, unlike metals, is a better conductor hot than cold, and the hotter it is, the better conductor it becomes. Carbon, however, even at a very high heat, is still a poor conductor, and it is impossible in actual practice to avoid some loss in the electrode itself. In all conductors, the longer the conductor, the greater the loss, but this loss can be lessened by increasing the size of the conductor. This same rule applies to electrodes, and in order to avoid all losses to the greatest extent possible the current should enter the electrode at a point as near as possible to the point where it will leave it. It is quite common practice to connect the metallic conductor to the head of the electrode, but this is a grave mistake, as the loss in volts in a long electrode will be from 4 to 6, depending on the current density employed, and in a furnace where the operating voltage is 50 volts, this

loss would be equal to from 8 to 12 percent of the total energy consumed. Electrodes should be held in the same manner as one would hold a bar vertically in the hand, so that they can be taken at any point on their length, and in smelting furnaces the holder giving contact to the electrode should not be at any time more than 1 foot (30 cm.) above the charge. As the electrode wears away it is slipped through the holder, and the process goes on until it is finally taken by the head, but at no time should the part of the electrode carrying the current project more than 2 ft. 6 inches (about 75 cm.) from the holder itself. The losses, both of heat and energy, can be decreased by increasing the size of the electrode, but this can be carried too far. The writer would recommend a current density of from 30 to 35 amperes to the square inch of section (5 to 6 per sq. cm.) in order to keep the electrode as cool as possible and thereby prevent side oxidation and heat losses. With too large an electrode, quite a good percentage of the total energy supplied to the furnace would be required to keep the electrode warm.

An important point, the value of which is sometimes overlooked when considering the size of electrodes, is that it is often advisable to use electrodes of greater cross-section than electrical necessity demands, but for a totally different reason. In some processes, for instance, the electrode when working is surrounded to a certain depth by charge mixture. At the surface of such charge mixture, and therefore at some distance from the working end of the electrode, inflammable gases are given off, and these burning in air tend to attack and consume the electrode. Thus there is a tendency to reduced cross-section at this point with consequent increased current density, followed by rise of temperature, which further aggravates the condition described. It is, therefore, wise, for convenience sake, to use a larger cross-section so that the burning away does not result in eating the electrode through, letting a large piece of electrode into the charge and disturbing conditions generally. This is one of the exigencies imposed by practice.

DISCUSSION.

DR. CARL HERING: I think it is well to hear from the carbon electrode makers on the practical side of this question of manufacture. In my opinion, the title of the paper is too general because it refers entirely to carbon electrodes and ignores entirely both graphite and metallic electrodes. There is a point about which I would like to have some information; is there any skin effect in these very large electrodes? In carrying a current of thousands of amperes in a 24-inch (60 cm.) electrode, it seems to me the skin effect might be quite noticeable.

MR. FITZGERALD: I think it may be shown that there is a skin effect. I have seen a large electrode get red hot on the outside, and be still black inside.

MR. HERING: That bears out the point I inquired about.

MR. C. A. HANSEN: It is true that if you take a large electrode you will find better conductivity at the surface than at the heart of it. I think it possible that the effect noted by Mr. FitzGerald is due more to higher specific conductivity at the surface of the electrode on account of the increasing concentration of binder-carbon towards the surface during the baking process. The specific resistance of carbon, and even graphite, is so great that skin effect should not enter perceptibly into consideration at 60 cycles in the case of 8 or 10 in. (20-25 cm.) diameter electrodes. At the usually lower frequencies, skin effect would be even less noticeable.

MR. FITZGERALD: What Mr. Hansen says as to better conductivity at the surface than at the center of large electrodes is quite correct, in my experience, as regards extruded carbons.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

GAS CIRCULATION IN ELECTRICAL REDUCTION FURNACES.

By Jos. W. Richards.

Mr. J. A. Leffler's splendid report on the working of the Trollhättan furnace in the electrical reduction of iron ores, presented at the Annual Meeting of the Jernkontoret at Stockholm, Sweden, May 31, 1911, occupying over 200 pages of that Society's Transactions, brings out more information as to the electrical reduction of iron ores than has ever before been available. The report has been discussed at length before this Society by Mr. T. D. Robertson (Volume XX, page 375), and also by Mr. Otto Frick, in *Metallurgical and Chemical Engineering* (December, 1911, page 631). A discussion of the results and of the devices employed brings into prominence the question of circulating the gases in such an electric shaft furnace, a device which has been employed by the Aktiebolaget Elektrometall for the last three years. The writer has some reflections to offer upon this subject, which may be preceded by a short discussion of the reasons for the adoption of this circulation.

Reasons for Circulating the Gases.

In the early working of the Domnarfvet furnace, the weakest point was the overheating of the roof of the crucible. To preserve this roof, Messrs. Groenwall, Lindblad and Stalhane conceived the idea of bringing from the top of the furnace some of the waste gases, and injecting them, comparatively cool, into the space beneath the arched roof of the crucible and charge beneath, so as to cool the under surface of the arch and thus preserve it from destruction. Later some of this cool gas was also employed to pass through the bronze castings, forming jackets through which the electrodes passed, thus cooling them thoroughly and sending into the furnace the heat absorbed from them, instead of losing said heat in cooling water.

Incidentally to the use of the cool waste gases, it was found

that when these gases were thus returned into the crucible of the furnace, in amount equal or superior to the volume of gases being generated by the reduction of the ore, this additional volume of gas carried out of the crucible into the shaft of the furnace above a considerable amount of heat, thus prolonging upwards the hot zone of the furnace, and increasing considerably the amount of reduction of the ore by CO gas in the shaft of the furnace. Indeed, without this circulation of gases the amount of gases produced by the reduction alone in the crucible was insufficient to heat the shaft of the furnace to any considerable distance, thus rendering the shaft useless as a place of reduction of the ore by ascending gases. The circulation was then pushed to an extreme, such that two-thirds to three-fourths of all the gases passing out at the top of the furnace was returned to the crucible, and thus virtually the same gas passed two or three times through the charge; the effect of this increased circulation was a pronounced economy and advantage, viz., increased heating of the shaft by the carrying upwards into it of surplus heat from the crucible, that is, a better distribution of the crucible heat upwards into the shaft of the furnace, and finally a better ratio of CO_2 to CO in the furnace shaft gases, showing that much reduction of ore has been accomplished by CO gas in the upper part of the furnace, and thus the ultimate goal of better utilization of carbon in the furnace was attained.

The writer is convinced, however, that these advantages are offset by serious disadvantages. The most obvious disadvantage is that the moisture of the charges and the CO_2 of the flux and the CO_2 gas naturally produced in the furnace are returned in large part to the crucible, and there act upon the unconsumed carbon, by the reactions

$$CO_2 + C = 2CO$$
$$H_2O + C = H_2 + CO$$

This very materially cools the smelting zone of the furnace, its most vital working part. The constructors and operators of these furnaces have recently introduced dust-catchers to intercept fine dust carried out at the top of the furnace by the gases, and also scrubbers, where the circulating gas is cooled, washed, and made to deposit this excess of water before passing into the

crucible of the furnace. This device certainly removes the dust and most of the water of the gases, but cannot remove the CO_2 which it is the aim of the circulating process to increase to as high a percentage as possible and thus economize the carbon of the furnace. It stands to reason, therefore, that the better the circulating system works in facilitating reduction in the furnace, that is, in producing more CO_2 in the gases, the more prejudicial will be the introducing of the gases into the crucible of the furnace produced by the chemical reduction of this CO_2 to CO. Besides, the circulating system is cumbersome and expensive, and soon reaches the maximum of useful effect; in the writer's opinion it is an imperfect solution of the difficulties of the furnace. Considering merely the reduction of the ore by CO gas in the shaft of the furnace, it is a question of temperature and time, and to a lesser extent of the amount of CO gas passing. The reduction in the crucible undoubtedly produces CO gas, which, rising upwards slowly through the charge, will have the very best opportunity of producing the maximum amount of CO_2 if it slowly filters upwards through the shaft and there has ore at a low red heat to act upon. If it were possible to keep the column of ore in the shaft of the furnace at a low red heat it is certain that the CO gas would perform the maximum amount of reduction possible, and pass out one-half or two-thirds converted into CO_2, thus consuming the theoretical minimum amount of carbon for reduction in the furnace. The critical point of this analysis is that the ore in the shaft and furnace cannot be maintained at a red heat by the ascending of the gas naturally produced by reduction of the ore; it is insufficient in amount. It follows that the reduction is facilitated either by maintaining the ore red hot by other means, or by circulating the gases two or three times through the ore, thus keeping the materials in the shaft at the reducing temperature. The latter scheme has been the only one adopted, and has been effective, but the extent of its advantages is largely self-limiting, as has been already explained. It is quite evident that when the amount of gas passing through the furnace is increased two or three times, its velocity is increased two or three times, and therefore it is in contact with the ore only one-half to one-third as long. Theoretically this would mean that there would be *no* increased reduction by CO,

except because of the higher temperature produced in the shaft by the increased volume of circulating gas increasing the velocity of the reduction reaction. The consideration of these circumstances leads to the following proposition.

Modified Working.

The writer thinks that the circulation of the gases should be entirely dispensed with, thus simplifying very greatly the operation of the furnace and regularity of its running. If this were done, means should be provided to preserve the arch of the crucible other than by injection of cool gas beneath it. I believe that the present experience of furnace men in preserving arches, ports and bridges of open-hearth furnaces by means of water-cooled plates embedded in the brick-work can be made to conserve the form of the arch of the crucible satisfactorily, thus dispensing with the necessity of introducing cool gas for this purpose. Then, having gotten away from the circulation of the gas, and the furnace again started in its original path, we can reduce the ore in the crucible by carbon and allow only the CO gas there produced to filter slowly through the charge in the shaft of the furnace.

In order that the ore in the shaft of the furnace may be reduced by gas it will be necessary to adopt other means of keeping the charge in the shaft of the furnace at a temperature above, say, 400° Centigrade. This can be done by means of auxiliary electric energy, and also conceivably by jacketing the shaft and burning the waste furnace gas around it.

I therefore suggest that the material in the shaft of the furnace be heated by the waste gases of the furnace burnt in flues around it, or by electric current passed through it from surface electrodes embedded in the walls of the shaft, at a point near the middle of the shaft, sufficient current being passed through the charge to heat it by its own resistance to a red heat. This will give the up-rising CO gas the maximum opportunity of reducing Fe_2O_3 and attaining equilibrium. In this way I believe that the following reaction can be attained,

$$5Fe_2O_3 + 9C = 6CO_2 + 3CO + 10Fe$$

representing the maximum formation of CO_2 by reduction in a slow current of CO. The above reaction requires only 200 parts

of carbon per 1,000 of iron reduced, which is much better than can possibly be attained by the present circulating system.

As above given, the reaction is based upon dispensing with the CO_2 of the limestone; that is, the limestone should be calcined outside of the furnace (which could also be done by waste gas of the furnace itself). This saves carbon by avoiding the evolution of CO_2 from carbonates in the lower part of the furnace, below the zone of reduction by CO gas, but where CO_2 is reduced to CO by solid carbon.

Conclusions.

(1) The arch of the crucible of the furnace should be protected by water-cooled plates, as is common in open-hearth furnaces.

(2) The artificial circulation of the gas in the furnace should be dispensed with.

(3) The limestone flux should be calcined before putting into the furnace.

(4) The shaft of the furnace should be provided with auxiliary heating to maintain its contents at or above 400° Centigrade, to permit of reduction of Fe_2O_3 by the slow current of CO gas.

(5) Under these conditions an amount of carbon equal to one-fifth of the weight of iron produced should be sufficient, producing gas containing two volumes of CO_2 to one of CO.

(6) Eliminating the expense of circulating and purifying the gas, and reducing the amount of fuel required for reduction, would both simplify and cheapen the operation of the furnace.

DISCUSSION.

THOMAS D. ROBERTSON (*Communicated*): Professor Richards has raised some interesting points in his able discussion of this problem of gas circulation in electric furnaces.

In the present Swedish practice the furnace gas contains CO_2 and CO in the proportions approximately of one volume of CO_2 to two volumes of CO, and comparing this gas with that produced

by the ideal reaction given in this paper, namely, two volumes of CO_2 and one volume of CO, one finds that the amounts of carbon necessary to give these two mixtures, and reduce the same weight of iron, are in the ratio of 15 to 9. Could the ideal equation be brought about it would result in a saving of about $2 per ton of iron, using charcoal costing in Sweden $15 per ton: or where coke at $5 per ton is used, a saving of 67 cents per ton of iron produced.

The circulation of the gases, whilst resulting as shown in a consumption of charcoal considerably in excess of that theoretically required under ideal conditions, has proven successful in preserving the roof and the upper walls of the furnace hearth. Were the gas circulation dispensed with for cooling purposes, some water-cooling device, as suggested, would have to be substituted, the success of which is open to doubt. Probably if water-cooled blocks or plates were embedded in the roof they would weaken it, be a source of danger from leakage, increase the weight, and, further, owing to the decreased pressure under the roof, due to the absence of the circulating gas, the chances of the roof giving way when worn thin would be increased.

It would appear, however, that the potential heat energy of the gases produced might to advantage be used in increasing the temperature of the charge in the shaft either by heating the ore before charging or by the method suggested in this paper. The proposed use of auxiliary electric heating might be found to be more cumbersome and expensive than the present gas circulating apparatus, and, further, would not be utilizing the heat which could be obtained from the burning of the gases.

At present, the tendency of Scandinavian practice seems to be towards a design which will enable the furnaces to run as long as possible without having to shut down for repairs, which involves very serious loss, especially when power is contracted for by the year.

Toronto, March 22, 1912.

PROF. DORSEY A. LYON (*Communicated*): Professor Richards speaks of the circulating gases having been passed through the electrode jackets. Although this was attempted, I understand that it was not successful, and for two quite obvious reasons:

(*a*) Gas or air being comparatively poor conductors of heat, the cooling of the jacket in this manner is not very effective.

(*b*) The CO_2 in the circulating gases, introduced in this way, might in contact with the hot electrodes act very destructively upon them by reason of its oxydizing effect.

Reduction in Stack by means of Circulating Gases: It seems to me that the tables given in Leffler and Odelberg's report show that no great amount of reduction could have taken place in the shaft of the furnace, since none of the recorded temperatures, except possibly at the very base of the shaft, are sufficiently high to have brought about reduction.

I quite agree that the effect of returning to the crucible ⅔ to ¾ of all the gases passing out of the top of the furnace is advantageous, because in this manner the surplus heat from the crucible is carried up into the shaft of the furnace, and it no doubt brings about a better ratio of CO to CO_2 in the furnace-shaft gases, but I do not think that this proves "that much reduction of the ore has been accomplished by CO gas in the upper part of the furnace," for as I have before stated, an examination of the table of Leffler and Odelberg's report, in which are recorded the temperatures which were taken in the shaft, shows that at no point except possibly at the very bottom of the shaft, were the temperatures high enough to effect reduction.

Disadvantages of Present System of Gas Circulation: The disadvantages are obvious, and so there is no need of discussing them. Further, considering merely the reduction of the ore by CO gas in the shaft of the furnace, I agree that it is a question of temperature and time, and to a lesser extent of the amount of CO gas passing. Such being the case, it is then a question of how best to attain this condition, that is, to raise the charge in the stack to a sufficiently high temperature to effect its reduction, its passage down through the stack giving the requisite time for the reduction to take place. I agree that by circulating the gas two or three times through the ore, as is done at present, the above may be accomplished, but it seems to me that this scheme is only partially effective, and that it is accompanied by the disadvantages mentioned. However, I do not believe the "modified working" scheme proposed would prove entirely

satisfactory. Attempts were made at the plant of the Noble Electric Steel Co. in California to preserve the roof of the crucible by water-cooled plates embedded in the brick work, but these did not prove especially effective. The furnace was also operated without the circulation of gas, but the results were not entirely satisfactory, although the furnace was operated for a considerable time in this manner. I quite agree that it will be necessary to adopt other means than those now employed, for keeping the charge in the shaft of the furnace at a temperature sufficiently high to effect reduction, and believe that this could be done by means of auxiliary electric energy, and that the jacketing of the shaft and the burning of the waste furnace gases around it would be of great assistance. However, in any modified system which I might suggest, I would not advise the elimination of the gas circulation. To my mind the ideal scheme would be to take the gas from the top of the shaft just as is now done at Trollhätten, and treat it as follows:

1st. Pass it through a "Cottrell System," for the removal of the solid particles in the gas, such as coke or charcoal dust, particles of ore, flux, etc.

2d. Through the circulating fan.

3d. From the fan through a regenerator filled with coke and heated electrically to such a temperature as to bring about the reduction of the CO_2 to CO. The gas at the same time would be heated, but not to such a high temperature but that it would still absorb heat as it entered the crucible and thus pass up into the shaft at such a temperature as to readily effect reduction.

4th. The burning of a part of the excess waste gases in a jacket around the shaft of the furnace so as to prevent radiation losses from the charge in the shaft.

5th. The passing of the waste gases from the jacket and the complete combustion of the same in a preheater, *whereby* the lime rock of the flux would be calcined and the total charge, minus the reducing agent (which is added afterwards) is raised to a sufficiently high temperature to permit of the iron oxide being reduced as soon as, or very shortly after, it is introduced into the stack.

The obvious advantages of such a system would be:

(*a*) The doing away with the introduction of water vapor into the gas, as is done by the present system of scrubbing it.

(*b*) The removal of CO_2 from the gas.

(*c*) The raising of the temperature of the circulating gas.

Of course I realize that the system as above outlined would be just as "cumbersome and expensive" as the present method, but probably no more so, and on the other hand more effective.

As for the method proposed by Dr. Richards, it seems to me that the possible objections to the same are:

1st. The non-circulation of the gas, thus allowing an accumulation of dead heat, as the furnaceman expresses it, in the crucible, just beneath the roof of the same, where it is not needed and does positive harm.

2d. The trouble and difficulty of maintaining an auxiliary system of heating the charge in the shaft.

3d. The lack of comparatively rapid circulation of gas through the charge, which I believe to be necessary to bring about effective reduction of the ore.

I trust that I have made myself clear and that I have not proposed anything impossible.

Mr. Assar Grönwall (*Communicated*): For a long time our attention has been directed to the difficulties now mentioned in this paper concerning gas circulation in our electric pig-iron furnaces, and we reached conclusions resulting in patent applications for

1. Heating the shaft by means of electric contact plates.

2. Pre-heating the charge by combustion of more or less of the furnace gases.

3. Eliminating and utilizing the CO_2 of the circulating gases, so that gas free from CO_2 is returned to the furnace.

However, we have not yet reached a practical solution. We really have more confidence in the third proposition than in the auxiliary heating of the shaft above 400°.

By reducing rich ore containing no carbonates, and using dry fuel, the gas circulation has given little trouble while its advantages have been increased. Even though there are CO_2 and H_2O

in the gas, its circulation appears better than none at all. No doubt it would be better to eliminate CO_2 and H_2O from the ore by preliminary calcination. We have used burnt lime in the furnace instead of unburnt, but the dust annoyed the workmen and we have returned to using the unburnt limestone.

Aktiebolaget Elektrometall,
Ludvika, Sweden, March 26, 1912.

Mr. J. A. Leffler (*Communicated*): It has been of the greatest interest to me to take note of Prof. Richards' paper, and I can certify the correctness of the reasoning which has led him to his conclusions. My experience at Trollhättan may, however, give me the right to submit them to a scrutiny, and when doing so I will handle them in the same order in which they are mentioned by the author.

1. From a practical point of view I cannot see any obstacle to protecting the roof of the crucible by water-cooled plates, and I think that cooling in this way can be done very effectively. But the drawback is that this kind of cooling actually deprives the furnace of a large quantity of heat, in the cooling water; on the contrary, the cooling by gas on the inside of the roof means only a removal of a certain quantity of heat from the crucible, where it does harm, to the mass in the shaft, where it will be of use.

2. If the artificial circulation of the gas in the furnace could be dispensed with, nobody would like it better than those who have to take care of the furnace; but, at least for the present, I cannot see how we can do without it. To my mind there is no better and more economical way for transferring the heat from the crucible up into the furnace shaft, and I wish to point out that the circulating gas must be regarded simply as an heat conveying agent. It depends on the capability of the circulating gas to take up sufficient heat to the mass in the furnace shaft, whether reduction by CO will take place and CO_2 be produced in greatest quantity. Meanwhile, the object with the gas circulation can be properly attained only if the charge (charcoal, ore, etc.) put in the furnace is perfectly dry. I have not had an opportunity to run our furnace in Trollhättan in that manner, but it would no doubt be of very great advantage to fuel-economy, *viz.*, cause a

high percentage of CO_2 in the gas, even if the gas-circulation be relatively slight.

As the most serious disadvantages of the gas circulation, the author points out that some carbon in the crucible is consumed by the H_2O and CO_2 in the circulating gas, by the reactions

$$H_2O + C = CO + H_2.$$
$$CO_2 + C = 2CO,$$

and that this causes a rather considerable cooling of the crucible, the most vital working part of the furnace.

As for the H_2O, I wish to say that the amount of water in gas at 15° C. is rather small, say 13 grams per cub. meter in the Trollhättan furnace, corresponding to about 15.5 kg. water per 1,000 kg. of iron. To decompose this 15.5 kg. water by carbon will consume about 40 kilowatt-hours, *if really the whole quantity will have time to be broken up.* Analysis of the gases indicate that this is not the case. The same argument applies to the CO_2. Howsoever those reactions effect within a certain limit a useful consumption of heat in the crucible, exactly counterbalanced by as large a gain of heat in the shaft, when H_2O and CO_2 are regenerated there. Through these reactions one gains an additional action brought about *chemically,* assisting the distribution of heat in the furnace which the gas circulation occasions *physically,* always provided that said circulation is kept within a certain limit. The lack of heat in the crucible can on all occasions, as you will understand, be well looked after by the electric current.

3. We have tried to use calcined limestone in the Trollhättan furnace but were obliged to give it up. It seemed that the lime was slaked by the wet rising gases in the furnace shaft, and then, of course, expanded to the threefold volume. Otherwise I do not see how to explain the fact that we had slips when using lime, but that those slips came to a stop immediately after changing from lime to raw limestone. It would be of great value for the economy of the process if calcined limestone (lime) could be used, but our experience up till now has told us, that the disadvantages are larger than the advantages, and we cannot but rely on our experience.

4. To arrange the furnace in such a manner that the mass in the shaft is heated up by electric current or by burning some of the gas outside the furnace fire brick wall, seems to me not to be practical from a constructive point of view. As before said, I think the best way is to use dried charcoal and dried ore to gain such a temperature in the furnace shaft, that the reduction with CO will reach a maximum.

Regarding (5) and (6), I have nothing specially to say.

Before ending my little contribution to the discussion, I beg to add a few words.

In an article by Prof. Richards in "Proceedings of the Engineers' Society of Western Pennsylvania," Vol. 27, No. 4, May, 1911, it is predicted that in a very few years the blast furnaces of Sweden will all be shut down, and electric pig-iron furnaces be running in their places. I myself have never had such a thought, and now there is still less reason to think so, having all the experience from Trollhättan as a basis for my judgment. Pig-iron produced in the electric furnace of the Trollhättan type costs a great deal more than was prophesied some years ago. On the contrary, such pig-iron turns out so expensive that electric pig-iron furnaces can only exist where the conditions are specially favorable. For instance, in Sweden we have some places where electric pig-iron process of the Trollhättan type can be made use of to great advantage.

Stockholm, April 1, 1912.

C. B. Morgan (*Communicated*): We offer the following comments as the consensus of opinion of our staff on Prof. Richards' paper:

1. We think there is no doubt but that the roof can be protected with proper water blocks. However, if the roof is so protected the heat losses would be greater than could be tolerated.

2. "The circulating system is cumbersome and expensive; it is an imperfect solution of the difficulties." As applied here and in Sweden, it is only a question whether the fuel saved warrants the expense and trouble.

3. Limestone flux should be calcined before being put into the furnace.

4. We do not think it feasible to provide auxiliary heating of the charge in the stack, as suggested, as the physical and mechanical conditions do not, in our judgment, permit of such process being carried out.

In our present type of electric furnace, which was installed early this month, we have dispensed with the circulation of gas and have used calcined limestone only as flux, and no reduction takes place in the stack.

We are making gray iron regularly, the analysis of which is:

Silicon	2.75 to 3.00
Graphitic Carbon	3.00 to 3.50
Phosphorus	0.018 to 0.028
Sulphur	0.011 to 0.016

Noble Electric Steel Company,
San Francisco, March 30, 1912.

MR. F. A. J. FITZGERALD (*Communicated*): As I understand the subject, the original object in using gas circulation in the Trollhättan furnace was for the purpose of saving the roof of the crucible, and a virtue has been made of this necessity. Unless there is a greater temperature than is necesary for the most economical working in the top of the crucible, any cooling device must be objectionable, particularly if it involves carrying off the heat in water. Water-cooling is absolutely necessary in some parts of some electric furnaces, but this should be avoided. Except in special cases a calorie derived from electricity is bound to cost more than a calorie derived from fuel, therefore, when using electric heat it is even more important to save calories than when using fuel heat. Carrying off calories in water should always be a last resort. It is for this reason that the working out of improved refractory materials is of such immense importance. If the roof of a furnace fails on account of the high temperatures to which it is exposed it should be built of more refractory materials.

For some months past our laboratories in conjunction with the Norton Company have been making a careful study of certain refractories, among which are bricks made of pure silicon carbide. These will stand excessively high temperatures and are also

resistant to the corrosive action of lime vapors. The use of these in electric steel furnaces has been particularly good so far, because it is possible to run the furnace at higher temperatures than can possibly be used without ruining a roof built of ordinary refractories, and, what is equally important, allows of bringing the roof much closer to the bath, thus effecting an important saving in the amount of energy required to attain and maintain a given temperature.

Naturally, the objection raised to special refractories is that they are apt to be expensive, but the important economic question is this: How much refractory material can be purchased with the value of wasted electric energy?

PROF. J. W. RICHARDS (*Communicated*): I wish to thank the gentlemen and firms who have shown the courtesy of discussing my paper.

The attempts of the Elektrometall Company to improve the circulation by the costly expedient of removing the CO_2 and H_2O from the gases proves how pressing a question is on hand for solution. It also proves that the better the furnace works, as regards producing CO_2 and thus economizing fuel, the more difficulties are placed upon the proper working of the circulating system.

I cannot agree with Mr. Leffler that merely drying the charges before putting into the furnace will add greatly to fuel economy by causing a high percentage of CO_2 in the gas. The saving of heat absorbed in drying will be something, but that will not increase CO_2 in the gases; the real saving will come from thus diminishing the H_2O in the circulating gases, and thus diminishing the oxidation of carbon by this moisture in the crucible of the furnace. Moreover, all the hydrogen gas thus produced is not re-oxidized in the furnace; there is over 10 percent of hydrogen in the issuing gases, and this represents a considerable net heat loss to the furnace. This is but another argument for suppressing the circulation of gases, if any other means of preserving the crucible roof and heating up the shaft can possibly be devised. The same principle applies to the CO_2 circulated and reduced to CO in the crucible. Only one-fourth of all the CO formed in the furnace is oxidized to CO_2 in the shaft; therefore only one-

fourth of the heat absorbed in the crucible by the production of CO from CO_2 can be considered as regained in the furnace by oxidation of CO to CO_2 in the shaft.

As to Mr. Leffler's opinion that electric pig-iron furnaces will not, in a few years, displace blast-furnaces in Sweden, his last sentence rather weakens this conclusion; because, since there are some places in Sweden where the electric furnace "can be made use of to great advantage," these places will soon be putting Swedish blast-furnaces out of commission.

The Noble Electric Steel Company says that the circulating gas system warrants its expense and trouble by the savings it effects. This is taken for granted; otherwise they would not use it. But it is nevertheless true that the system has very serious and inherent limitations, which are in principle unavoidable, and that it is very well worth while to try to effect the desired savings by other more effective and less-inherently-limited devices.

Mr. FitzGerald's remarks are very much to the point. If the crucible roof can be made to stand without gas- or water-cooling, then I feel certain that the clumsy and (in principle) faulty device of gas circulation will be quickly abandoned.

Lehigh University, April 16, 1912.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

FURTHER DEVELOPMENT OF ELECTRIC FURNACES FOR HEATING BARS AND BILLETS.

By Thaddeus F. Baily.

In a previous paper before this Society, the writer described the development of an electric furnace for heating bars and billets, and gave data from tests made at that time. This paper will describe the development that has been carried on in this branch of electric heating since the tests mentioned above.

In September, 1911, The Electric Furnace Company, the organization controlling the furnaces described, installed adjacent to the power house of The Stark Electric Railroad Co., at Alliance, Ohio, a laboratory for testing and demonstrating the furnaces to be later described.

The equipment is housed in a special building constructed by the Electric Furnace Co., and affords adequate space for the necessary tests and demonstrations.

The electric equipment consists of a 200 K. V. A., single-phase, 400-volt to 20-volt transformer, a switchboard with radial switches, and the necessary volt, ampere, watt, power factor and recording watt-meters, as shown in Fig. 1. The temperature measurements are made with a Brown platinum-rhodium couple indicating pyrometer, mounted on a bracket adjacent to the switchboard.

The first furnace constructed was lined with chrome brick and chrome ore, and had a rated capacity of 60 kw. with a designed voltage of 110. The furnace was run for a period of 12 days, and a marked lowering of voltage was noted from day to day, beginning with 150 volts, 400 amperes, when the furnace was started, and dropping gradually until on the eighth day the voltage had to be reduced to 20 volts to permit the kilowatts to go about 60.

This irregularity of electrical conditions was, of course, not

permissible, so the furnace was cooled for examination. On inspection it was found that the chrome lining had fluxed with the coke, making a material extremely hard and tough to break when cold, although at furnace temperature (3000° F.—1650° C.) this material was a pasty mass. Further, the thermal efficiency of this furnace was very poor, running less than 30 percent,

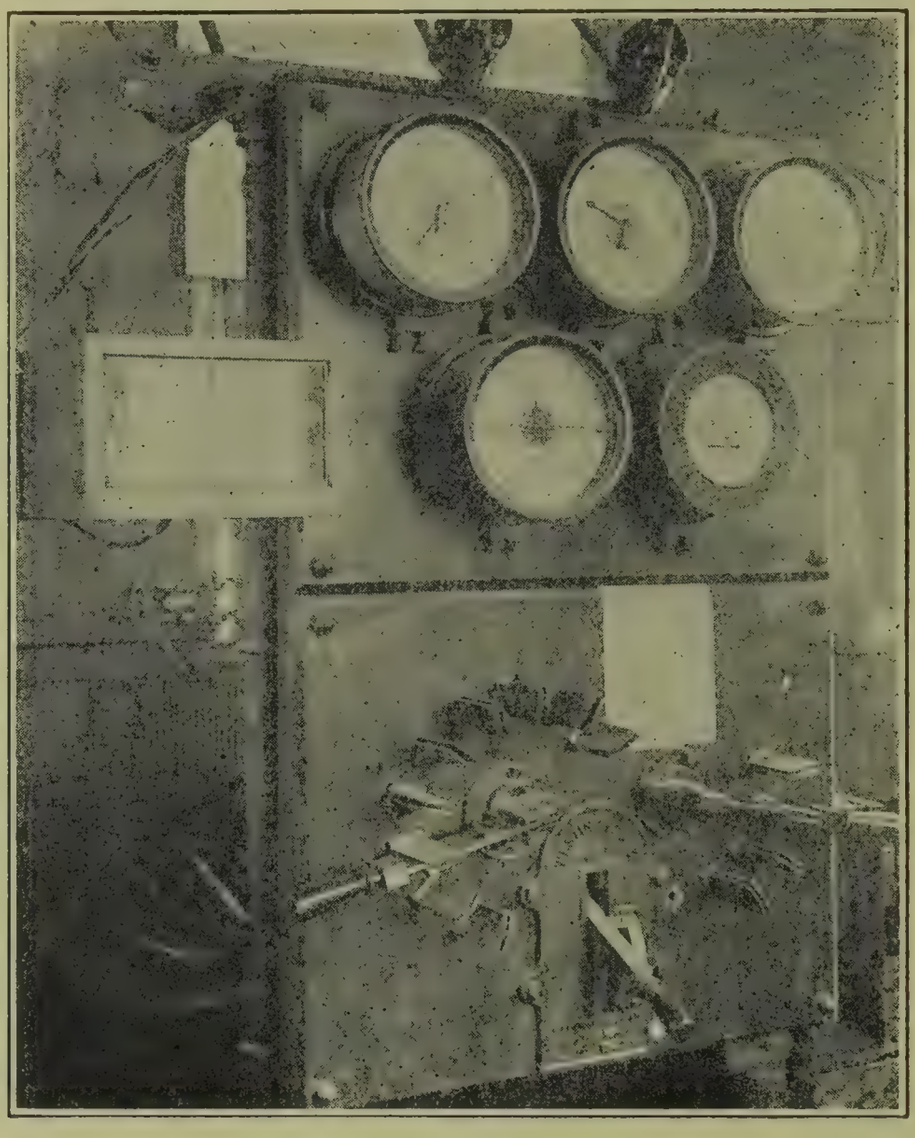


FIG. 1.—Instrument Board.

which was due in part to the use of fire-clay brick for the furnace walls, these walls being 20 inches (50 cm.) thick.

As it was obvious that chrome was not the material for lining, its use was abandoned, and two new furnaces of 15 kw. capacity each were constructed, the first with a silica brick lining, the second with a lining of Grecian magnesite brick and ground Grecian magnesite. These furnaces were run for a period of

10 days each, at varying current consumption ranging from 10 to 50 kw. Both linings held up well, and while furnace temperatures of over 3200° F. (1760° C.) were maintained at times in each of the furnaces, neither lining completely failed during the run. The Grecian magnesite lining withstood the temperatures better and did not flux with the carbon core, while the silica lining fluxed slightly; consequently the magnesite lining was fixed upon for use in the larger furnace now to be more fully described.

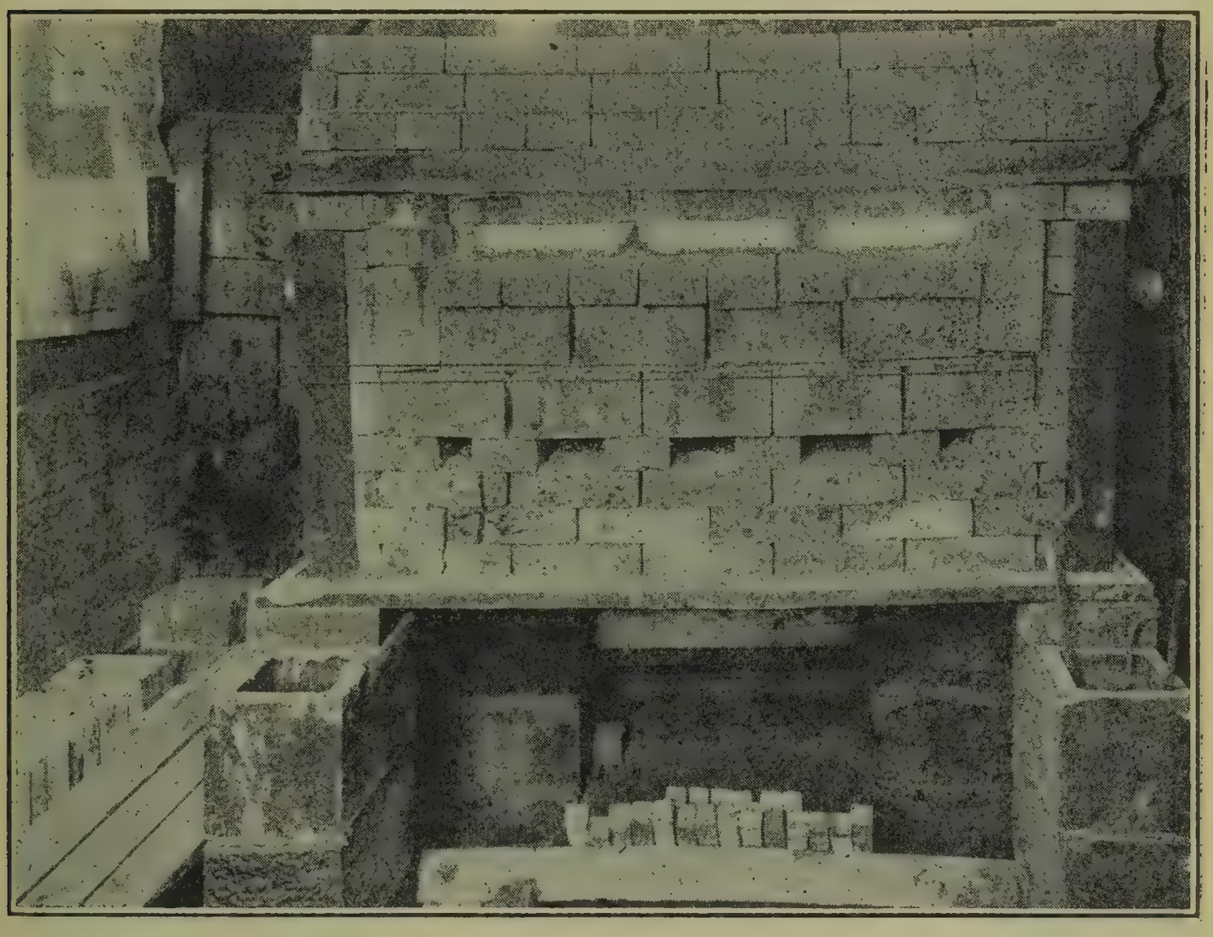


FIG. 2.—Front View of Furnace.

The dimensions of this furnace, as shown in Fig. 2, were 56 in. (140 cm.) wide, 45 in. (113 cm.) front to back and 42 in. (130 cm.) high, and it was designed for 60 kw. current consumption when heating 240 pounds (109 kg.) of metal per hour. The wall loss was calculated at 30 kw. per hour. These figures checked very closely, as the wall loss with a ruling temperature of 2650° F. (1455° C.) was 28 kw. and the metal heated was 280 pounds (127 kg.) with 66 kw. in one hour's time, this giving a figure of 4 pounds (1.73 kg.) of metal per

kw. hour. The metal was raised from a temperature of 50° F. (10° C.) to 2350° F. (1288° C.). Under the above conditions the furnace had a thermal efficiency of approximately 50 percent.

The voltage of this furnace was entirely satisfactory; from a starting voltage of 150 volts the voltage was rapidly reduced to 60 volts, the current flowing at this voltage with a temperature of 2650° F. (1454° C.) was 1,000 amperes, with power factor 0.98. This current and temperature condition was maintained for hours at a time when heating metal. When no metal was

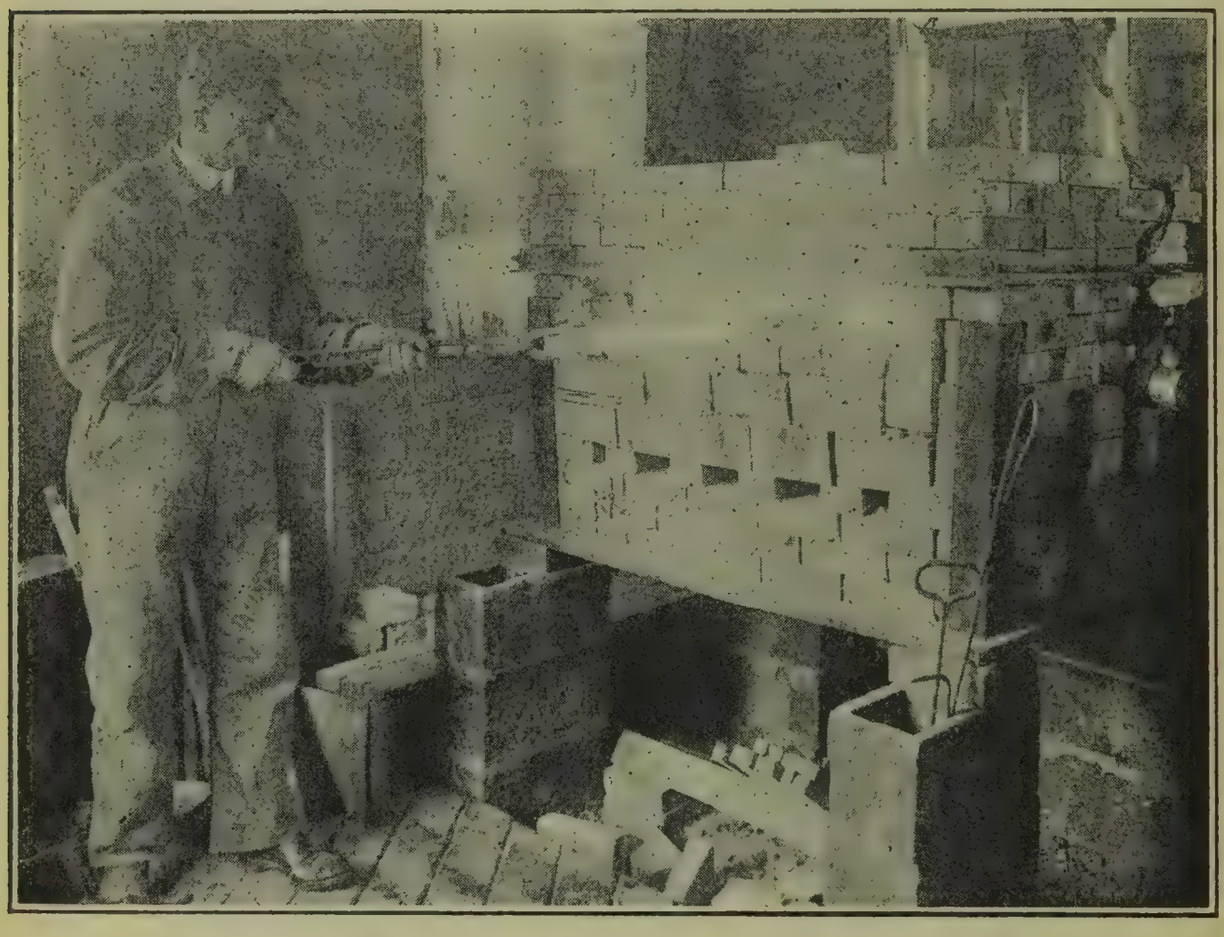


FIG. 3.—Side View of Furnace in Operation.

being heated, the current was reduced to 46 volts, 600 amperes, with power factor 0.98, and the temperature in the furnace maintained at 2650° F. (1454° C.) as previously mentioned.

When this furnace had been run for 13 days, the top was removed and the interior inspected, and the following observations noted:

The contact between the resistance body and the electrodes was perfect, there being no arcing or trouble of any kind.

The contact between the electrodes, which were 4 x 4 in.

(10 x 10 cm.) carbon, and the stranded feeder-cables was made with bronze clamps and Dossert cable-lugs, and gave no trouble whatever.

A tendency of the electrodes to burn at the point of entering the furnace walls was corrected by using two 3-in. (7.3 cm.) round electrodes in place of one 4 in. (10 cm.) square, and placing a sheet iron sleeve over the outer end of these electrodes to a point at least 8 in. (20 cm.) inside the furnace walls. The clamps were then placed over the sleeve and electric connection made from clamp to electrode, the current going through this protecting sleeve. This arrangement effectually prevented the oxidation of the electrodes at this point.

The electrodes in contact with the resistance material showed no reduction in size whatever—in fact, were of slightly increased size, owing to particles of the carbon resistance material adhering to the electrodes.

The coke or resistance material, composed of ½ to ⅜ in. (0.6 to 0.9 cm.) crushed coke, was completely converted into graphite, and lay in a compact though not hard mass in the core of the furnace.

The Grecian magnesite lining had eroded to a depth of about 1 in. (2.5 cm.) on sides and bottom, where in contact with the coke, but had not fluxed with the coke at all. This lining was then repaired by adding a 2-in. (5 cm.) layer of Grecian magnesite, mixed with water, so that it would hold to place until the resistance material was put in. On heating the furnace to temperature this magnesite cintered into place without trouble. Since this repairing, the furnace has run about 30 days with great regularity, and the linings are apparently in excellent condition.

The cost of the magnesite for such repairing as noted above was about $2.00, and required about 3 hours' time for one man to do the work. This low cost of repairs was exceedingly gratifying as compared with the high cost of refractory repairs in oil furnaces.

The data given below were taken from a typical test sheet showing the current conditions and metal heated during a given period:

Temperature of interior at charging	2615° F. (1435° C.)
Temperature of interior at withdrawing	2600° F. (1426° C.)
Voltage of furnace	60
Amperage of furnace	1150
Power factor	0.99
Indicated kilowatts	69
Amount of metal charged, being 8 bars 1½ in. (3.8 cm.) square by 18 in. (45 cm.) long	92 pounds (41.7 kg.)
Time in furnace	20 minutes
Temperature of metal, when charged	60° F. (15° C.)
Temperature of metal, when withdrawn	2360° F. (1239° C.)
Kilowatt hours consumed in heating metal	23
Pounds (kg.) of metal per kilowatt hour	4 pounds (1.73 kg.)
Kilowatt hours per ton of metal heated	500
Capacity of furnace, per hour	276 pounds (125 kg.)

DISCUSSION.

PROF. JOS. W. RICHARDS: The last table of data given in Mr. Baily's paper shows an efficiency calculated at about 40 percent of the heat of the electric current put into the bars, and I do not doubt but what with better planning of the furnace and better insulation that figure can be nearly doubled. If the heating of the bars is done with a means which supplies the heat more rapidly the heating can be done more efficiently and with more satisfactory results.

If, for instance, the bars are placed with their sides at 45° to the horizontal, and not laid flat, they should expose more surface to the radiant heat and become heated more quickly. If they could be superficially smoked, as in a smoky natural-gas flame, their absorptive power for the radiant heat might also be greatly increased. Has Mr. Baily made any such experiments?

MR. T. F. BAILY: Regarding more rapid heating, I think that this is not desirable from an operating standpoint, as the rate of heating now used is about as rapid as is considered good for the steel, and a more rapid heating would call for a higher ruling temperature in the furnace and hence a greater heat loss.

As to placing the bars with their sides at an angle of 45°, I think that this is not desirable from an operating standpoint, as the heater would probably object to this extra attention in placing.

Regarding smoking the bars before heating, this also would be interesting, I believe, only as a laboratory experiment, and not commercially successful.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

TEMPERATURE MEASUREMENTS ON THE SILICON CARBIDE FURNACE.

By L. E. Saunders.

A carbon-lined iron bowl and a carbon rod in the hands of Acheson turned out a few crystals of silicon carbide, some twenty years ago. It is instructive to reflect that in this tiny experiment, using a feeble electric current, there existed the same limitations of temperature that are found in the great commercial furnaces used for making this product today. That there are comparatively narrow temperature limits has been long recognized by those operating commercial furnaces. But neither in the tiny experiment just mentioned nor in the latest commercial forms of furnace has it been known what these limits are, below which crystalline SiC will form and above which it ceases to exist.

It is not strange that this information has seemed unobtainable during the many years in which the knowledge that there existed temperature limitations has been practically applied. It is only quite recently that the development of means of temperature measurement has reached the point where the refinement of the instruments gives such assurance of accuracy at the high temperatures involved as to warrant the effort to overcome the obvious difficulties involved in getting at the information desired. But these means are now at hand and our only excuse for remaining longer in ignorance are the obvious difficulties just mentioned. What these have been found to be will be quite fully described, for this paper is an account of some experiments in measuring temperatures of the furnaces at the Chippawa, Ontario plant of Norton Company, where silicon carbide, called Crystolon, is made.

It is obvious that the only principles of temperature measurement available are the so-called optical or radiation methods, as the ranges are mostly beyond other pyrometric means, and the

optical and radiation instruments, as is well-known, are profoundly affected in their readings by the presence in the field of vision of any vapors. As the temperatures are greatest on the inside of this furnace, some means must be adopted to reach that

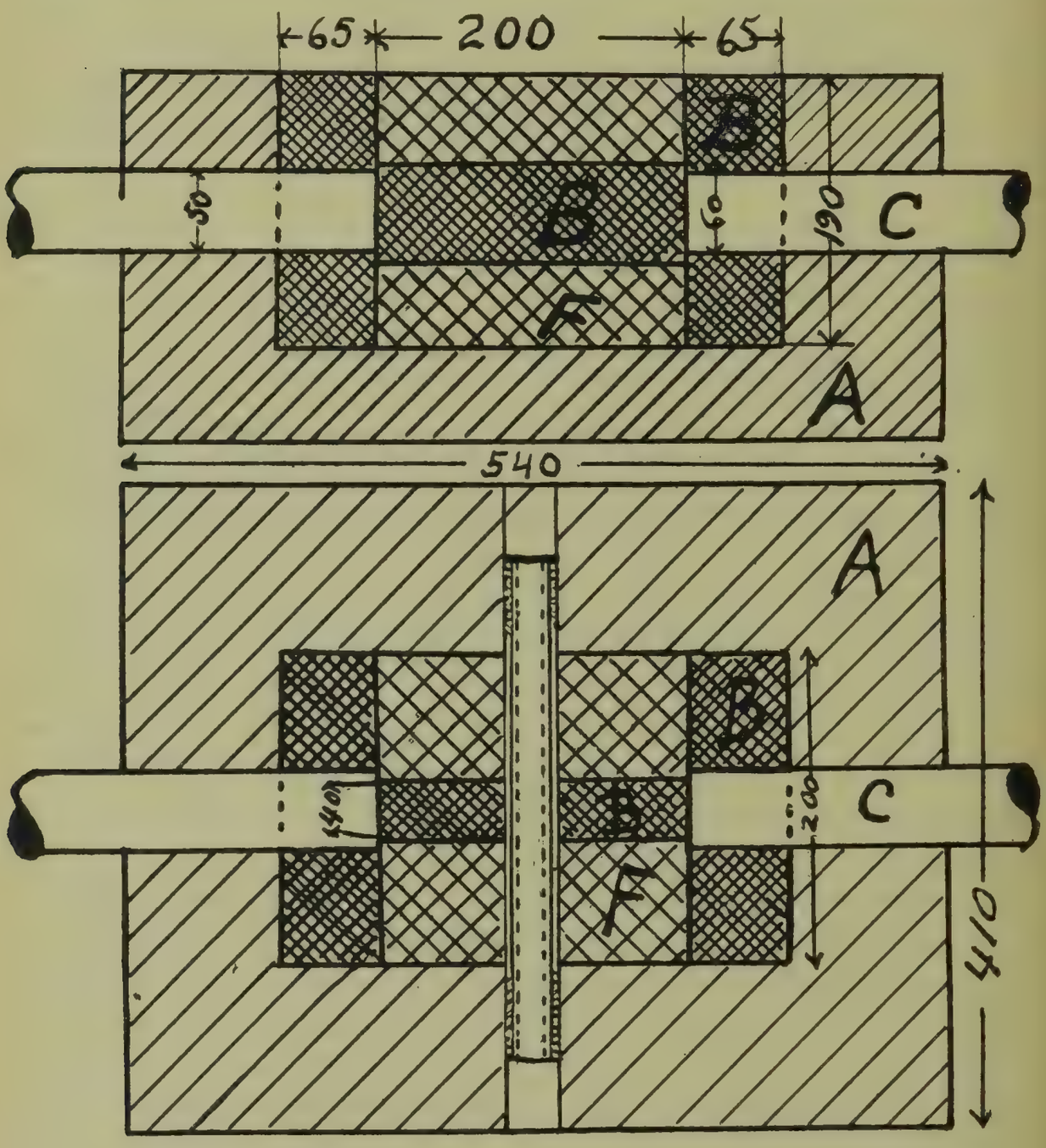


Fig. 1. Tucker and Lampen's Furnace.
(dimensions in millimeters.)

position with fumes or vapors eliminated. A tube at once suggests itself, with some appliance for removing or keeping out the fumes with which the interior of this furnace is well supplied.

Some earnest efforts to dispel the gloom surrounding the subject have been made by various workers, but the earlier endeavors

were all along the line of forming crystalline silicon carbide in some other way than from a heated mixture of silica and carbon, or involved some laborious observations such as density determinations of carbon heated in the various zones—all coming back to the final necessity for measurement of the actual temperature used.

The first published account of experiments on such a plan with a commercial mixture appeared in 1906 in the Journal of the American Chemical Society, and described the work of Tucker and Lampen on a furnace with the following dimensions: Length 330 mm., width 200 mm., depth 190 mm., the core being powdered coke and rectangular in shape, 40 mm. wide by 60 mm. deep. A graphite tube 330 mm. in length, outside diameter 25 mm., and bore 18 mm., was placed transversely through the furnace and core, and was sighted into from both ends with a Wanner pyrometer.

While the results obtained may have some claims to accuracy, the description of the method, in fact the method itself, does not offer much assistance in attacking the subject from the commercial standpoint. It is difficult, if not impossible, to get a tube which will traverse the commercial furnace from side to side, and no mention is made of fume difficulties or a way to overcome them.

A more elaborate and systematic research was conducted at Cornell University by Mr. H. W. Gillett, under the direction of Prof. Bancroft and was described in the Journal of Physical Chemistry for March, 1911.

Briefly stated, his finally-adopted method was to use a tube, itself made of silicon carbide, with a double wall, one end closed with a graphite disc, this end being placed against the core on the side, the other end projecting through the brick walls of the furnace. The two tubes used, one fitting inside the other, had these dimensions: Outer tube 64 mm. outside and 44 mm. inside diameter, and 300 mm. to 450 mm. long; the inner tube 38 mm. outside and 25 mm. inside diameter, length the same as the outer tube. A small carbon tube was inserted at the outer end between the two tubes and the remainder of the space between filled with a refractory cement. A graphite disc 4.7 mm. thick accurately fitted the inner end of the larger tube. When suction was

applied to the small carbon tube a draft was created drawing air into the inner tube from the open front end, and out between the walls of the two tubes, carrying away any fumes or vapors from the field of vision. The furnace for the work, after some preliminary changes, had the following dimensions: Length 685 mm., width 406 mm., and depth 380 mm., the core used being

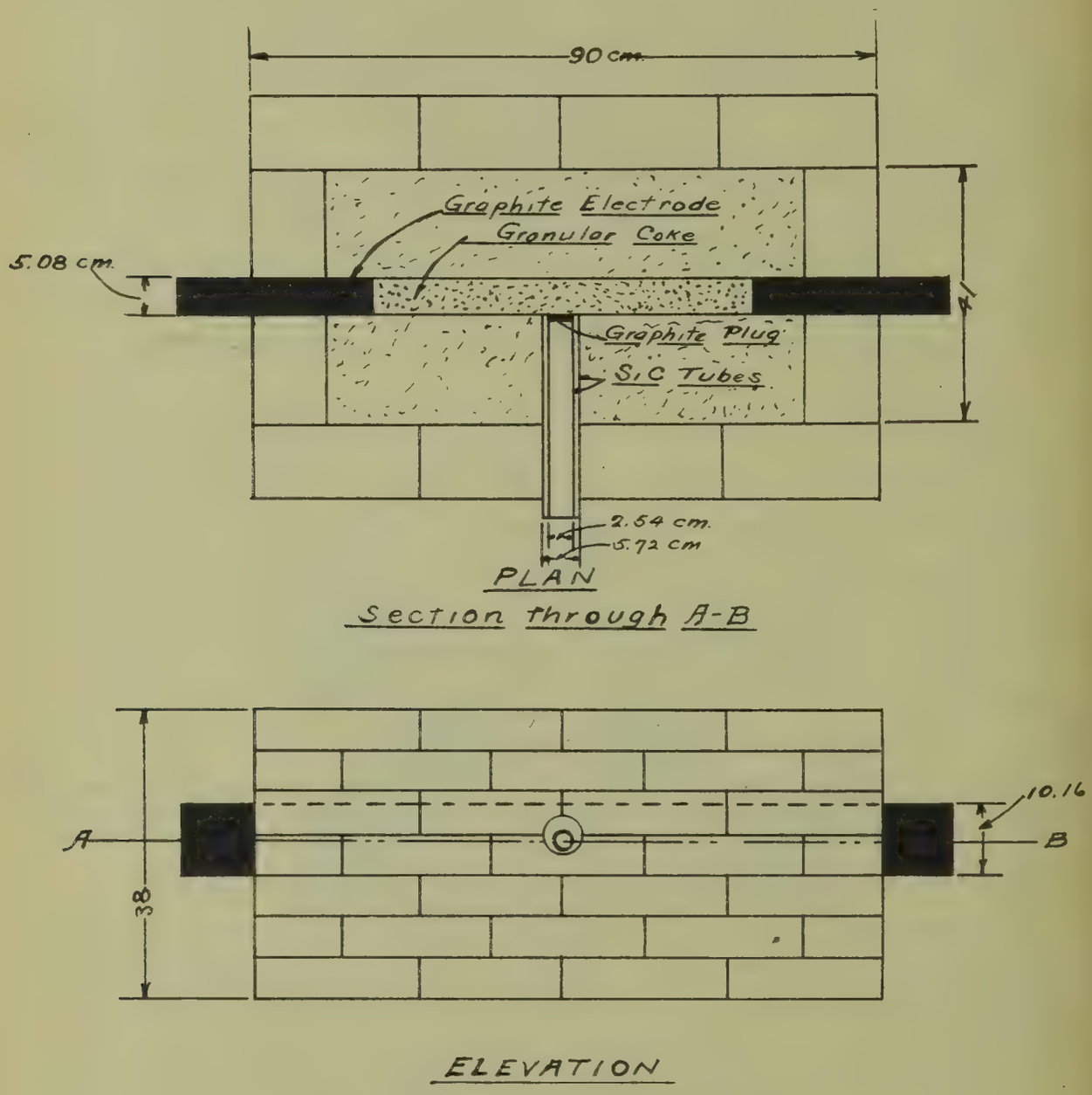


Fig. 2. Furnace finally used by Gillett.

rectangular in cross section 50 mm. x 100 mm. and composed of carefully sized granular coke. The tube was centered as nearly as possible in the furnace, which used energy to the amount of 50 kw. and held 68 kilos. of charge.

The precautions taken were so elaborate and the difficulties encountered and overcome so completely set forth, that we should

probably have undertaken the work at some time, even without the urgent suggestion of Prof. Bancroft. He has been so anxious to have results on a furnace of large size, to compare with the smaller ones and to learn what commercial value might result from a knowledge of the actual temperature conditions, that this work has been hastened for his especial benefit.

In passing from work on a small furnace to a large one, there are conditions to be met that are rather baffling. The greater distances to cover, the settling of the charge and the longer time of running, necessitate tubes of comparatively great length and strength, and of high resistance to thermal and oxidizing conditions. While Gillett finally chose silicon carbide tubes, because of greater general accuracy, he also worked with tubes of car-

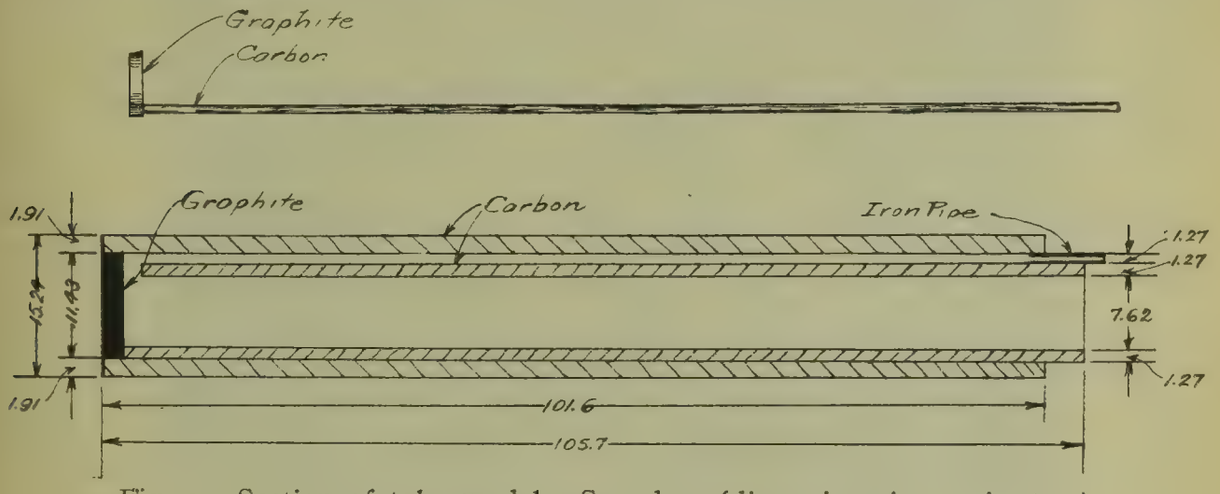


Fig. 3. Section of tube used by Saunders (dimensions in centimeters). Upper figure shows the movable plug.

bon and graphite. The choice of silicon carbide tubes was due to the desire to have as nearly as possible the same temperature gradient through the tube as occurs in the furnace. This is of course desirable, but is not absolutely essential to reasonably correct results, as will be shown. At any rate, the manufacturer of the small tubes ran into such great difficulties in making the larger ones required, that we were obliged to get on without them and use the next best thing, amorphous carbon. Even using this material the problem is not easy. The considerable distance of the core from the outside of the furnace walls required great length, and on account of this length a large diameter to furnish field enough for a pyrometer. In addition to length and large diameter, considerable strength was required, for the tube had not only to bear the burden of several feet (1 to 2 m.) of charge

above it, but also to stand the strain of having its inner and hottest end settle from 45 cm. to 60 cm., while the outer and cold end maintained its original level. Besides, one end came to an extremely high temperature with great rapidity while the other end and the greater part of the side walls were cold. That

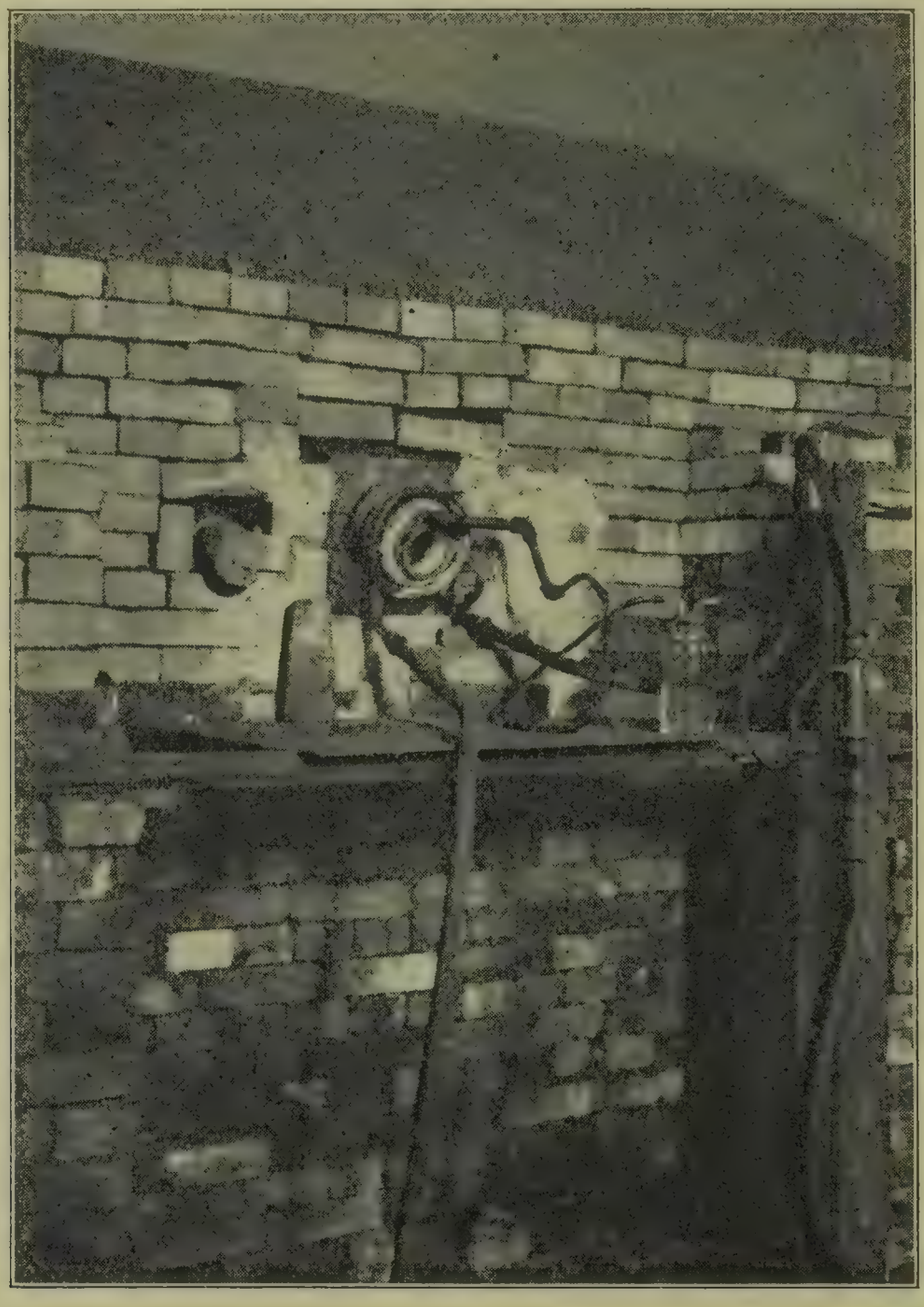


Fig. 4. Showing end of tube, in position, before the run.

carbon tubes stood such treatment at all speaks much for them, and that the breakage was less than one-third is remarkable. The tubes used, one of which is shown in Fig. 3, consisted of an outer one 100 cm. long, 150 mm. outside, and 114 mm. inside diameter, and an inner one 100 cm. long, 102 mm. outside and 76

mm. inside diameter. A piece of 12.7 mm. iron pipe was inserted at the cold end extending in about 75 mm. between the tubes, and the remainder of the open end space between the tubes sealed with a refractory cement, for a distance back of 38 to 50 mm. The end inside the furnace was closed with an accurately fitted disc of graphite 19 to 25 mm. thick, while a slot in the end of the inner tube which was close against the graphite disc, allowed communication between the inside of the inner tube and the space between the two.

The early experiments indicated that some means must be adopted to protect the outside of the tube at the furnace sides, for the gas flames played against it, eating through before a 36-hour run was completed. Large carbon blocks were first fitted around the tube for a distance of about 200 mm. and while these protected it from some burning, the most successful experiments were done with a coil of iron pipe around the outer tube, extending about 200 mm. back, through which cold water was circulated. This plan effectually prevented the burning of the tubes from the outside, and readings could be continued after the run was over if desired. The coil was embedded in a thick mass of firesand and pitch, which baked hard and furnished additional protection. Pipe fittings were screwed to the small iron pipe, extending it to a distance where rubber tubing could be connected without melting off. The rubber tubing was used to connect, through a wash bottle, with an ordinary laboratory suction pump.

Gillett carried on researches, which must have taken months, on the calibration and choice of pyrometers. As a result of his conclusions we made a choice of instruments without going to the labor and expense of making the actual experiments ourselves.

We have been working with a Thwing total radiation instrument, such as described by Dr. Thwing before the Franklin Institute in 1908, constructed with special scales for the work, and calibrated, through the kindness of Prof. Bancroft, at Cornell University against the standard instruments at hand there, as well as in actual use at Chippawa, by a borrowed certificated Wanner pyrometer.

It is outside the scope of this paper to enter into a discussion of the relative merits of pyrometers or the laws on which the

various instruments are based, but I would like to call attention to a difficulty in the calibration which someone may like to discuss. In reading temperatures with the two instruments (Wanner and Thwing) on a rising temperature scale, with only the rear plug heated, a different correction was obtained than when descending temperatures were read on a movable plug and with the side walls heated also. As the latter was the one used for the determination of the various zones, the difference did not

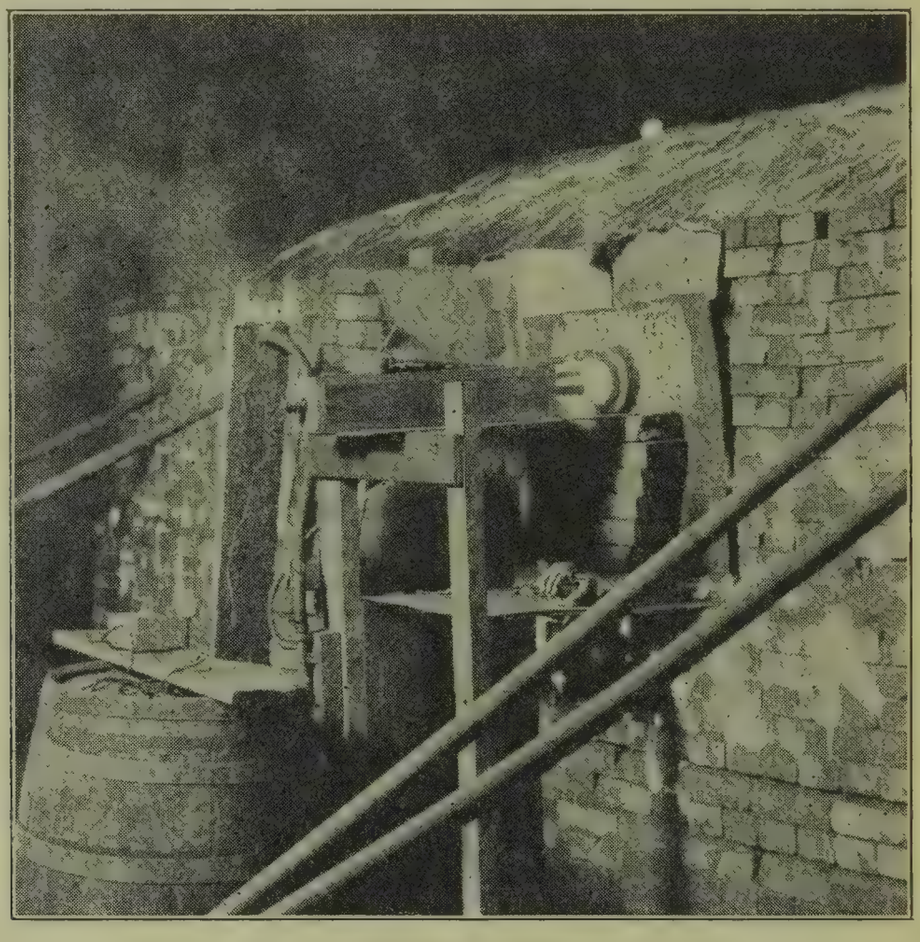


Fig. 5. Furnace during the run.

matter very much. Whether there is a departure from black-body conditions in either case, or a polarized-light condition, or an unusual amount of ultra-voilet or infra-red rays in the light, or what other condition has caused the difference, has not been a subject of investigation in these experiments.

It is not to be understood that the Thwing is the only pyrometer that could be used, but taking into account the working conditions, which are not the best in a dusty furnace room, and the expense, it seemed the one to choose. It has given consistent readings and good service under the most trying circumstances.

As has been mentioned, there are two scales, one reading to 2,000° C. from 1,200° C. and the other to 2,800° C. from about 1,600° C. It was found beneficial to surround the metal tube of the instrument with a wooden box to aid in a quick return of the pointer to zero, and to prevent the effect of outside influences on the thermo-couple through the sides of the tube.

Turning now to the experiments, readings were first attempted at the graphite disc next the core throughout a furnace run. The curve, Fig. 8, is typical of the results obtained. It will be noted that the temperature increment is rapid, but the readings at the lower points were shown to be low by means of an additional single tube inserted beside the other, with a small hole through which the heating of the core was observed. The difference in temperature between the inside and outside of the graphite disc lessens rapidly as the core heats up and as Gillett has shown the permanent heat lag becomes small at points above 2,000° C. and after the run has continued for some hours. Some curious effects have been noted. At a temperature of slightly over 1,940° C. the ray of light issuing from the tube takes a greenish color, more pronounced when the vapors are allowed to lie in the tube, and still deeper in color as the temperature goes up. The radiations have a peculiar effect on the bare skin. If they are allowed to play on the face or hands a smarting or tingling is observed somewhat different from a burning sensation and without sensible heat. This becomes particularly annoying in taking readings with an optical instrument where the face must be held for some time in the direct path of the rays.

In tubes which have cracked in the early stages, and most of the breakages have occurred within an hour of the start, vapors have entered and formed beautiful crystal effects. Occasionally tubes have filled solidly, and as the temperatures have increased the crystals have decomposed in the hotter portion leaving a beautiful skeleton of carbon, while farther on in the tube the Crystolon is still intact, interspersed with globules of ferro silicon. When a tube breaks, vapors at high pressure rush from the front end and burn with a brilliant yellow flame to a great height, the products of combustion condensing in fluffy particles composed of complex and variable silicon compounds.

When the suction was cut off (it was found advisable to use

it as little as possible on account of burning) the tube filled with heavy fumes almost instantly, so dense that the tube could be looked into with the naked eye. These swept out rapidly, however, as soon as the suction was applied.

Changes in core area, or in other words changing the rate of energy developed per square mm. of core area, has had less effect than was expected on the core temperature. With areas varying as much as 5 percent the variation from the average in the maximum temperature reached has not been more than 50° C.

Fig. 6. Showing end of tube, in position, after the run.

although as was expected the larger core areas gave the lower temperatures. At different points on the core some change has been noted. Near the furnace terminals a zone of slightly higher temperature has been observed, but this is also a small difference.

In addition to reading temperatures at the core, numerous readings have been taken at various distances out through the furnace charge. This was done with a separate graphite disc, slightly smaller than the inner diameter of the tube, which was attached to a thin carbon rod, by means of which it was moved

to the desired position. With this appliance we were able to determine the points at which fire-sand begins to form, at which crystalline silicon carbide forms, and at what temperature it decomposes into its constituent elements.

Before discussing the actual temperatures found, the possible sources of error should be considered. In reading at the core, the permanent lag through the disc may cause a low reading. Gillett found that there was a difference of 17 degrees at 2,160° between the two surfaces of a 4.7 mm. thick disc. It is thought however, that this difference becomes less with longer time and at higher temperatures. At the early part of the run this lag, as has been mentioned, is rather great, but the shape of the curve indicates that the difference lessens very rapidly. Another possible source of error at the rear plug is the effect of air currents. Again Gillett has shown that little or no correction is required on this account. He has also stated that there is practically no departure from black-body radiation if the graphite disc be given a matt surface. The most serious source of error is the heat carried out by the tube. An examination of the sides of the tubes when the furnace is opened shows that the various products are pushed out at the tube farther than in the furnace. Gillett again comes to the rescue with a determination of the deviation from true temperatures using a carbon tube. He finds 30° as a fair figure to deduct from readings at any point in a carbon tube. In connection with and really a part of this error is the cooling effect of the water-coil around the front of the tube. In making runs with the coil and without it no difference in temperature at the core was noted. In as much as it was impossible to carry a run through without the water-cooling device, we had to make the best of it and use the readings obtained. These sources of error do not enter in reading core temperatures.

In reading on the movable disc, the heat carried from the hotter portions of the furnace by the walls of the tube works against the lag due to the walls of the tube itself, as does the water cooling at the front. But as the points desired are taken from the walls of the tube rather than from the different zones in the furnace product itself, the error is almost entirely overcome if sufficient time is given the disc to assume the temperature of the

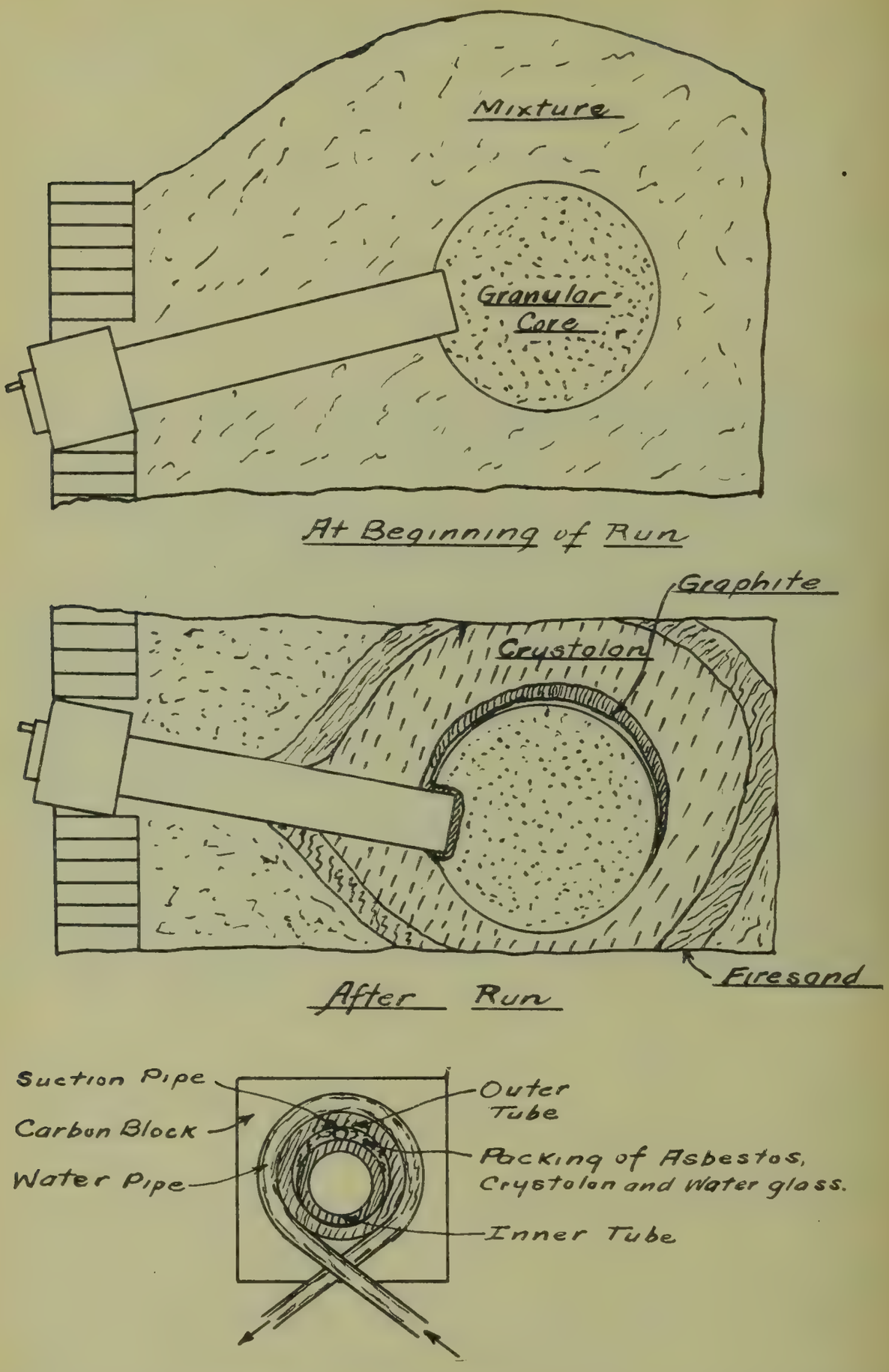


Fig. 7. Showing original and final positions of tube in furnace, and method of cooling its front end.

point at which it is placed. At least, I made no allowance for an error on this account.

In getting temperatures of the various zones, considerable time is consumed on account of the small movement of the disc each time and the necessity of allowing it to assume the temperature of the new position. To test for error here, a position was taken which had been read two hours earlier and the temperature was found to have varied only 10 to 15 degrees and this at 1,950°.

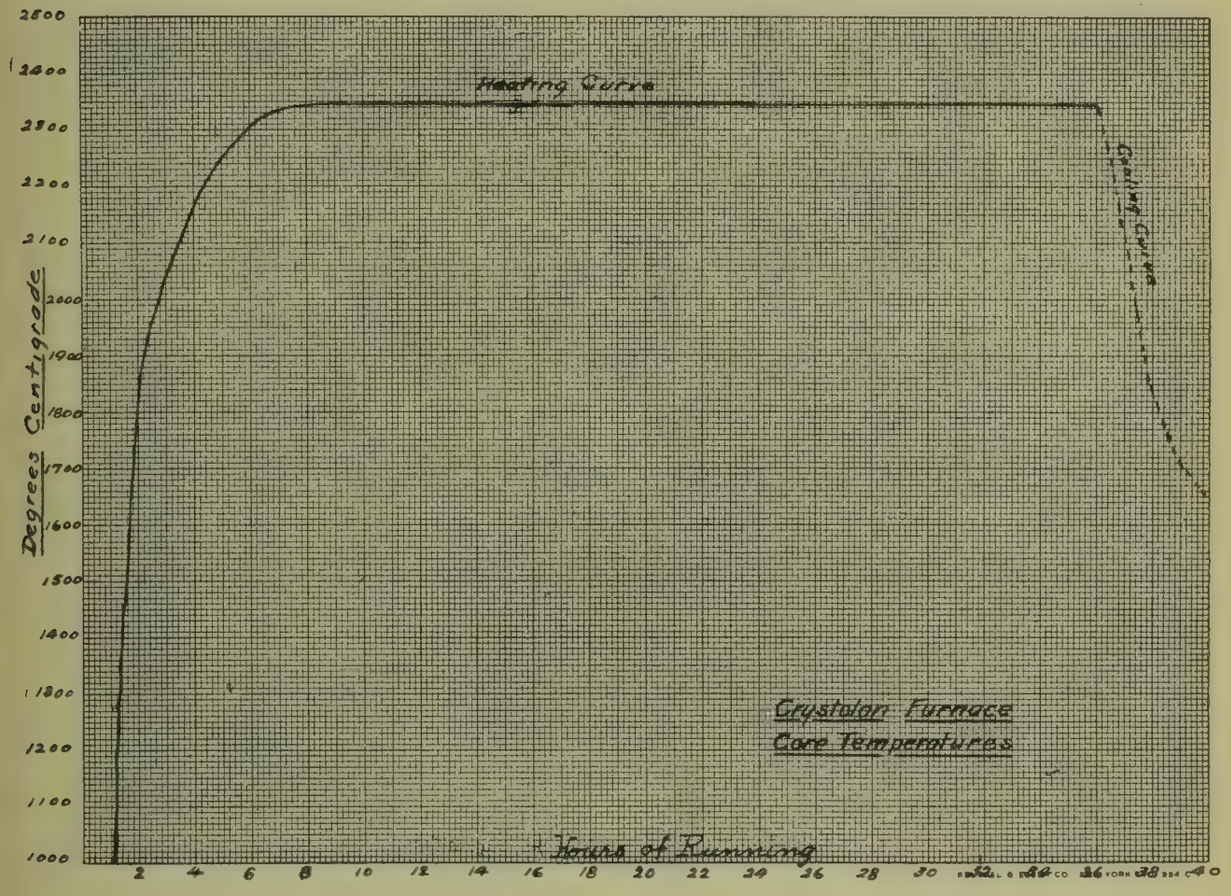


Fig. 8. Curve of core temperatures during and after furnace run.

Various guesses have been made as to the temperatures prevailing in this furnace. Acheson gives 7,000° F. (3,870° C.) for the formation point of silicon carbide and 3,500° to 4,000° F. (1,927° to 2,204° C.) for fire-sand. Moissan gave 3,400° C. as the decomposition temperature of silicon carbide. Many other estimates are in the same high range. Tucker and Lampen find for crystalline silicon carbide the decomposition point to be 2,220° C. and the formation point 1,950° C.; Lampen gives about 1,600° C. as the formation temperature of fire-sand.

Gillett applies some corrections to these figures. He assumes

the 2,220° point for decomposition to be accurate but applies corrections making the readings 1,500° for fire-sand, and for silicon carbide 1,830° C. Gillett's own results, with all corrections applied, are, formation point fire-sand 1,540° ± 30°, formation point crystalline silicon carbide 1,820° ± 20°, and decomposition point of silicon carbide 2,220° ± 20°.

An average of our results, with the greatest departure from it given as plus or minus, are: Formation point, fire-sand, 1,600° ± 50°; formation point, crystalline silicon carbide, 1,840° ± 30°, and decomposition point of silicon carbide, 2,240° ± 5°.

No corrections other than the calibration of the instruments have been applied to these figures. The possible error in using corrections obtained from experiments on a small scale and applying them to the larger apparatus and longer time, is believed to be as great as using the actual results found. That these are in reasonable agreement with previous determinations indicates that the errors of observation are not great.

Many refinements are wanting in these experiments and the exact figures found may be open to some criticism, but the results have been capable of duplication and thus of practical value, and that was the chief aim in carrying on the work.

TABLE OF RESULTS.

	Fire-sand (Limits)		Crystalline Silicon Carbide, (Limits)	
	Formation °C.	Decomposition into Crystalline SiC	Formation °C	Decomposition into C and Si
Tucker and Lampen, 1906 .	1600	1950	1950	2220
Same, corrected by Gillett .	1500	1830	1830	2220
Gillett, 1911	1540 ± 30	1820 ± 20	1820 ± 20	2220 ± 20
Saunders, 1912	1600 ± 50	1840 ± 30	1840 ± 30	2240 ± 5

I desire to make grateful acknowledgment to Prof. Bancroft for advice and assistance, freely asked but as freely given; to Mr. J. R. Griffith for much of the hardest work, involving many sleepless nights; and above all to the Norton Company, at whose expense the researches have been made and by whose courtesy these results are made public.

DISCUSSION.

MR. GEORGE K. BURGESS (*Communicated*): It is certainly a tribute to the skill of Mr. Saunders as an experimentalist, that with the large commercial furnace with which he is working, he is able to so control its behavior that he can reproduce very exactly the temperature conditions and measurements of previous observers using the small laboratory furnaces.

He appears to have demonstrated that it is possible to maintain pyrometric control, on a commercial scale, of a chemical process running at over 2,000° C. and confined between relatively narrow temperature limits.

The total-radiation pyrometer for use at such high temperatures possesses the single advantage, often of great importance, however, of being self-registering and recording; whereas the optical pyrometers are less affected in their readings by variable emissivity from the furnace, fumes, size of aperture, and stray radiation. Other things being equal, one would expect to obtain, with the greater facility, more exact estimations of temperatures of 2,000° C. and over with one of the instruments using a single color. There is no difficulty in calibrating accurately such an optical pyrometer, to as high temperatures as can be attained, while the satisfactory calibration of a total-radiation pyrometer is beset with many uncertainties. This, however, does not prevent the use of the total-radiation instrument to regulate high-temperature operations, independently of the actual scale of temperatures it may indicate.

If it is considered desirable to delimit the silicon-carbide reaction-temperatures with great exactness, this could probably be best done in such a furnace as the Arsem vacuum furnace, using perhaps Kanolt's method of taking the time-temperature curves of small samples on heating and cooling with an optical pyrometer, by which method the location of any transformation giving out or absorbing heat is easily recognized.

In the furnace of Mr. Saunders there could hardly be any polarization affecting the readings of a Wanner pyrometer, and the observer may easily be protected from heat and glare by a suitable shield. If the Holborn-Kurlbaum pyrometer (the Ger-

man form of the Morse Thermogage) be used, it is possible, with this furnace of large aperture, for the observer to be fifteen or more feet distant from the furnace. There have been recent improvements in the monochromatic and absorbing glasses suitable for use with such instruments, so that there need be no hesitancy in using them when properly calibrated.

Bureau of Standards,
Washington, D. C.

DR. R. B. SOSMAN (*Communicated*): The temperatures are for the most part outside the range of the Geophysical Laboratory, since our work on the silicates lies almost entirely between 1,100 and 1,700°. The part of most interest to us is naturally the basis of calibration for the temperature scale. Was the certificated Wanner pyrometer calibrated by the Reichsanstalt or by the Bureau of Standards? The Reichsanstalt has been in the custom of calibrating these instruments only to 1,400°, so that the scale beyond this point is merely an extrapolation of the scale of the instrument. The Bureau of Standards sometimes calibrates these to higher temperatures.

The Wanner is a very satisfactory and reliable pyrometer, especially when new, although after long use it sometimes gets off rather badly. The Thwing total radiation pyrometer I have never used, and so have no experience as to its reliability.

The temperature scale itself has been defined, strictly speaking, only as far as the gas-pyrometer investigations of this laboratory and of the Reichsanstalt have been carried; namely, to 1,600°. However, the study of the laws of radiation above 800° permits the scale to be carried to much higher temperatures than 1,600°, but, it should be remembered, with a constantly increasing error.

The statement of the decomposition point of silicon carbide as 2,240° $\pm$ 5° is therefore a statement of the reproducibility of the actual observations, and not of the accuracy of the temperature, a point which seems to be stated with sufficient clearness on page 434 of the paper, although it is very often overlooked by users of pyrometers bearing scales which can be read within a few degrees.

The paper as a whole covers a remarkably successful piece of

work on a problem offering very considerable technical difficulties, and I have been very glad of an opportunity of reading it and comparing the results with those obtained by Gillett a few months ago.

Geophysical Laboratory,
Washington, D. C.

PROF. W. D. BANCROFT: These experiments bring out very clearly two things: The identity between measurements on a small scale and on a larger scale, and the difference between them. With Tucker's 12-kilowatt furnace, Gillett's 50-kilowatt furnace, and Saunders' 750-kilowatt furnace, the temperature measurements are absolutely identical. On the other hand, although the principle of the method was given in Mr. Tucker's original furnace, Gillett and Saunders have modified it to meet special needs, and you get a considerable amount of discrepancy. There was a great deal of work necessary to be done before we could pass from the furnace of Tucker to that of Gillett, and Saunders had a great deal of work to do before he could get results. When it comes to the influence of temperature, you can determine that just as well on one scale as another; but, of course, you must rearrange your type of measuring apparatus to fit each furnace with which you have to deal.

DR. R. AMBERG: I would point to one similar experience which I had. For instance, one would expect that conductive material should conduct heat away from the furnace, and consequently show a crystallized zone somewhat distorted towards one side of the axis of the furnace; but experience from Mr. Saunders' and many previous experiments shows the contrary. As the second diagram in Fig. 7 indicates, the formerly concentric boundary lines between the crystals, the green stuff, and the unaltered mix bulge towards the outside where the graphite tube is inserted. This seems to be due to the difference in electric conductivity between the mix and the inserted body and also to the contact resistance between the two. It appears, therefore, that the marks on this graphite tube do not allow of determining the thickness of the layers of the various furnace products.

DR. C. B. THWING: In regard to the pyrometric discrepancies, it would seem to me that the simple explanation is that the graphite disk is not a black-body. It follows the black-body law, but the constant of radiation is lower than that of a black-body.

There are two ways in which you can have black-body conditions; one is a black-body, the other is a body enclosed in a furnace. A black-body is one which absorbs all the radiations which fall upon it, reflecting none. Such a body radiates as much heat as falls upon it, and radiates the same at a given temperature whether it is in the open or enclosed. On the other hand, a body which is not a black body reflects a part of the heat, for example 10 percent. Such a body would radiate in the open nine-tenths as much energy as a black-body, at the same temperature. In a uniformly heated, closed furnace, however, both bodies would radiate exactly the same, since the body which absorbs 90 percent of the energy and reflects 10 percent would send to the instrument reflected radiation from the walls of the furnace equal to 10 percent of the total radiation from the black-body.

In the case under consideration, while the temperature is rising the graphite disk is hot and the tube is cold. If the graphite disk radiates but 90 percent, the pyrometer readings would be low; after the tube has become heated, however, the conditions approach more nearly those of a closed furnace, and some of the heat from the walls of the tube is reflected by the graphite disk, thus making the readings higher.

PRESIDENT WHITNEY: We know that in the spectrum the same law holds. Is it not possible that you might have the Frauenhofer effect in measuring the temperature, heated vapors forming absorption bands? You describe the green color; might not that be due to the fact that you have taken out by absorption some of the other colors? Some forms of radiation pyrometers might thus give erroneous readings.

MR. L. E. SAUNDERS: That would not be true in an instrument using only monochromatic light.

PROF. S. A. TUCKER: I would like to know whether Mr. Saunders has done anything with the sublimate condensed from the fumes in those experiments. There should be a fairly

large quantity of material which might be examined and analyzed. We might expect to find the nitride of silicon there, which is quite an interesting compound.

MR. SAUNDERS: The fumes or vapors separated from some of the unsuccessful experiments are voluminous. We could collect a large quantity of these compounds. We have made some qualitative tests only on them. If Professor Tucker would like to make some analyses, we will furnish him with all the samples he requires.

DR. JOS. W. RICHARDS: Since the time I measured one of the first crystals of carborundum made by Mr. Acheson, I have been intensely interested in the theory as to how silicon carbide crystals are formed. The fact that crystals are here shown *inside* the graphite tube (indicating samples on table) confirms a theory which I have stated once or twice before. It appears certain that the formation of silicon carbide crystals is the result of two vapors coming together in the silicon carbide furnace, the vapor of silicon and the vapor of carbon. The vapor of carbon has a vapor tension somewhere between one-half millimeter and one millimeter of mercury at the temperature of the silicon carbide furnace, and we know that silica gives off vapors at low temperatures which could react in the formation of carborundum crystals. Or, as Dr. Whitney prefers to regard it, the silica vapors would become under these circumstances silicon vapor. These two vapors coming together seem to be the natural explanation of the formation of crystalline silicon carbide.

MR. SAUNDERS: In regard to this tube, brought here to show how the various zones were determined, if any one cares to examine it they can see where the different zones begin and end. The measurements of product zones were taken on this tube rather than in the furnace. The products were back further in the furnace than the lines on this tube indicate.

DR. AMBERG: I would like to say that the explanation given by Dr. Richards, is good for most of the cases, but there is another manner of formation of silicon carbide something similar to the cementation of iron by carbon. If you place a number of pieces of granular carbon into a silicon carbide furnace, you find the silicon diffused into the interior of these grains in cases

where the explanation just given would not hold. We may, however, assume that at the surface of the carbon the vapors of carbon and silicon combine to form silicon carbide, and that silicon under its own vapor pressure diffuses from here to the inside of the grain of carbon.

PROF. TUCKER: I think the explanation which Professor Richards made was clearly shown by Moissan years ago. He formed silicon carbide, by just that method, combining the vapors of carbon and silicon.

MR. SAUNDERS (*Communicated*): In order to bring this paper within the time limits allotted to it, it was decided to eliminate all reference to the theory and practice of the commercial silicon carbide furnace. For that reason I have not commented on some of the discussion which applies to other subjects than temperature measurement, although sorely tempted to do so. It is such a very large field and has been so frequently written about, that several papers might be advantageously given to various phases of the work.

Dr. Thwing considers that our tubes departed from black-body radiation. While this may be true, it is difficult to see how, in any commercial application of this pyrometer, black-body conditions could be more nearly approached. The graphite disc was always given a matt surface and at no time except at low and unrecorded temperatures was it alone heated. That is, the carbon tube was always hot for some inches back, which would tend to decrease the extremely small emissivity of the disc.

Mr. Burgess points out the difficulty of initially calibrating a total radiation instrument, and it would seem that this is the real explanation of the difficulty we had in our calibration.

Dr. Sosman casts some aspersions at Prof. Bancroft's Wanner pyrometer with Reichanstalt certificate, but in view of the careful work done by Gillett with identically the same instrument it is a refinement beyond the present work to question the accuracy of the instrument.

I am grateful to Dr. Sosman for emphasizing the fact that the close agreement of the observations at the decomposition point of silicon carbide is not intended to mean that the temperatures found are absolutely so exact, but that in several observations we were able to reproduce the readings within the given limits.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 19, 1912, President W. R. Whitney in the Chair.

VACUUM FURNACE METALLURGY.

By Colin G. Fink.

In practically all furnace processes in common use for the extraction of metals from their ores, the tension of the gases within the furnace varies but slightly from that of one atmosphere. The experiments recorded below were carried out with the idea of ascertaining whether ores, particularly complex or "rebellious" ores, such as smaltite, containing arsenic, sulphur, phosphorus or similar elements, could be more readily and more economically reduced in a vacuum.

Before the era of electric heating, vacuum furnaces for high temperature work were too cumbersome to become practical. In recent years, however, electric vacuum furnaces have been built on scientific principles and have worked most satisfactorily.

There are several furnaces of the Arsem type,[1] in daily operation at the works of the General Electric Co., varying in sizes up to 12 by 15 by 30 inches (31 x 38 x 76 cm.) in the heated zone. In my experiments with the Arsem furnace the absolute pressure maintained was always less than eight millimeters of mercury, and there was no difficulty in attaining it.

I. Experiments with Smaltite Ore.

This ore was particularly interesting at the time we started this research (1907), owing to the recent discovery of large beds of cobalt-bearing ore in Canada. The metal cobalt is little known. When free from arsenic it is very ductile and malleable. Some of the alloys have been studied. Alloyed with chromium it is used for fine cutlery, which is claimed to be non-corrodible.

[1] Trans. Am. Electrochem. Soc. 9, 153, 171 (1906).
Jour. Amer. Chem. Soc. 28, 921, 935.
U. S. Pat. 785,535; 1,009,625.
J. Ind. Eng. Chem. 2, 3.

Now that the metal can be bought for less than one-third of what it cost ten years ago, new uses are sure to be found.

Ever since the opening of the mines at Cobalt, Canada, there has been a demand for a practical method of separating the arsenic in the ores from the metals, in particular from Co and Ni. Various processes have been tried, such as roasting, leaching, etc., but without much success.

On this topic, Mineral Industry, 1906, 1910, contains the following:

"The smelting of the imported ores—from Canada and New Caledonia—is concentrated in the hands of the International Nickel Company, operating the Orford Smelter at Bayonne, N. J., and the American Nickel Works at Camden, N. J. The Orford Copper Company pays $30 per ton of ore containing 12 percent of Co and over, and $10 per ton containing 6 percent of Co and over. The Cobalt silver-ore bodies carry considerable cobalt, nickel and arsenic. The last two constituents are at present valueless to the mine owner, and he gets nothing for cobalt unless it is in excess of 6 percent.

"Owing to the high price of cobalt, the miners (at New Caledonia) are able to make a living from an ore carrying between 4 percent and 6 percent cobalt. The smelters who have bought these ores (from Cobalt, Canada) have not seen fit to give out any information, but the fact that they have allowed nothing for Ni, Co, or As is significant.

"To make even an attempt at a partial recovery of each of the metals is a long, tedious process and the most complicated from a metallurgical standpoint that has been presented for solution."

The use of the vacuum furnace suggested itself. After a number of trial runs which gave very promising results, I determined upon the following methods of attack, the idea being to gasify the arsenic in some way or other:

I. Heating the ore without any additions.

(a) below 1500°.

(b) above 1500°.

II. Heating with additions, such as $CaCl_2$, which would possi-

bly form volatile compounds with the arsenic or with such as CaC_2, which would bind the arsenic in the slag.

Some difficulty was experienced in the determination of arsenic in the ores and products. The presence of sulphur, antimony, silver and silica necessitated tedious and lengthy separations to insure accurate results. The first lot of ore contained 51.2 percent As and 19.7 percent of Co; the second lot assayed 48.4 percent As, and 21.3 percent Co. In analyzing the products, the peroxide method of Danzinger and Buckhout[2] was found to give very rapid and satisfactory results. The sample was finely ground and fused with sodium peroxide. After leaching and destroying the H_2O_2, the oxide of iron (from the crucible) was filtered off and the solution titrated with sodium hyposulphate, using starch iodine as an indicator. This D.-B method was compared with Pierce's and also with the gravimetric ($Mg_2As_2O_7$). Results showed that the D.-B. method was sufficiently accurate for our purposes.

The great advantage of the D.-B. method is the comparatively short time required, it being possible to make an arsenic determination in less than an hour, whereas the gravimetric method requires at least a day. A sample of the product of charge No. 323 was fused with Na_2O_2, and the clear solution divided into three equal portions. The results of the analyses are summarized in Table I.

TABLE I.

Portion	Method	As Found
I	Pierce	27.0 percent
II	Gravimetric	26.7 "
III	Danziger-Buckhout	27.7 "

[2] School of Mines Quart., **24**, 400.
Jour. Am. Chem. Soc., **25**, 535.

Method I: Heating Smaltite Without Any Admixtures.

The results may best be summarized in the following table:

TABLE II.

Smaltite No. 2.

Charge No.	Parts by Weight	Temperature C°	Time Hrs.	% As in product	Remarks
317	20	500	6	30.1	Loss in wt. 40%
319	50	850	3	29.4	Slightly sintered.
323	50	1,325	3	27.7	Magnetic alloy.
315	50	1,200	1½	29.5	Non-magnetic.
315	100	1,450	1½	29.5	Non-magnetic.
368	100	1,250	1		
		1,550	1½	25.4	Non-magnetic.
334	100	900	⅔		
		1,350	½	10.3	Magnetic.
		1,800	½		
343	25	1,000	½	6.6	Magnetic.
		1,800	½		

Up to temperatures of about 1500°, but 40 percent of the arsenic present in the ore is expelled. It is only after exceeding the melting-point of cobalt that a further reduction in the arsenic is brought about. At temperatures below 1450° we are dealing with a speiss which is very stable in vacuum. The first distillate of run No. 343 analyzed 97 percent arsenic. 1800° is too high for practical purposes and the loss of metal is excessive.

If silver is present in the ore, it distils out at about 1300° and can be collected in a chamber fitted into the cooler portions of the furnace.

Method II: Effect of Additions.

Since it proved difficult to reduce the ore by intense heating, I next tried the effect of additions. Of all those I tried the most effective was calcium carbide, or a mixture of $CaCO_3$ and carbon.

There are comparatively few compounds of arsenic that will readily form under the conditions of pressure and temperature of our furnace. The trichloride of arsenic boils at about 130°, and the trifluoride at about 60° under atmospheric pressure, and consequently a good deal lower in vacuum. The boiling or subliming points of the oxide and sulphide are not known.

It occurred to us that our difficulties in expelling the arsenic

might be largely due to the lack of porosity of the charge. We consequently prepared a mixture of three parts of ore to one part by weight of coke. The charge was gradually heated up to 1450° and kept there for a quarter of an hour, the total heating lasting about two and a half hours. The product was full of arsenic.

Our results are summarized as follows:

TABLE III.

Charge No.	Parts by Weight	Admixtures	Temperature	Time Hrs.	% As in Product
321	30	NaCl 30	950°	2¾	30.8 (S)
339	30	NaCl 30	700	2½	31.5 (S)
333	25	$CaCl_2$ 25	600	½	
			900	½	26.2 (S)
			1,500	1	
327	30	CaF_2 25	500	½	
			to 800	..	28.1 (S)
			1,325	2	
329	30	CaF_2 25	925	½	
			1,350	¾	30.2 (S)
			1,600	½	
341	30	Fe_2O_3 20	900	½	21.9 (S)
			1,200	2	
			1,500	½	
340	15	FeS_2 9	1,000	2	6.6 (S)
367	30	$CaCO_3$ 20	700	1	
		CaC_2 6.4	1,100	½	
			1,500	1½	2.1 (S)

Charge No.	Remarks
339	Non-magnetic beads.
333	Slightly magnetic beads.
329	Magnetic alloy.
341	Magnetic button.
367	Strongly magnetic.

Although the temperature in No. 321 was moderately low, no chloride of As was apparently formed. The sodium chloride distilled out of the crucible, collecting in fine crystals in the cooler portions of the furnace. Substituting for NaCl, $CaCl_2$, with its higher sublimation point, and running the temperature gradually to 1500°, did not alter the results materially. For all of the charges recorded in the table, carbon crucibles were used. A basic charge is preferable to a neutral or an acid one.

From the results obtained with fluorspar additions (Runs Nos. 327 and 329, Table III), it is evident that the arsenic cannot be expelled as fluoride, AsF_3, under the conditions we employed.

Our attempts to expel the arsenic as oxide or sulphide by admixing Fe_2O_3 (hematite) or FeS_2 (pyrites) have not met with much success so far. At all events, it does not seem possible to remove the arsenic readily either as As_2O_3 or As_2S_3

Run No. 367 was repeated a number of times and the results were invariably good. The temperature 1500° to 1550° being considerably below the boiling point of the metallic constituents at atmospheric tension the loss in metal was only a few percent, due very largely to spattering and the like. The underlying idea was to mix the ore with a reaction-mixture which upon heating yields a metal, or metals, whose heat of combination with the non-metallic elements contained in the ore is higher than that of the metal combined with said elements in the ore, in other words, yields a reducing metal whose affinity for the non-metallic elements is greater than that of the metal combined with them in the ore.

If, for example, a mixture of calcium oxide and calcium carbide is employed, the calcium oxide and carbide interact according to the following equation: $2CaO + CaC_2 = 3Ca + 2CO$. The liberated metallic calcium combines with the arsenic to form calcium arsenide according to the following reaction: $CoAs_2 + 3Ca = Ca_3As_2 + Co$. Calcium arsenide separates from the reduced cobalt as a slag, and part of the arsenic is volatilized.

Oxides and carbides of various earth metals or alkaline earth metals can be used in this manner, the most suitable reducing metal depending upon the character of the ore to be reduced. I consider the calcium oxide—calcium carbide mixture as typical and in case of most ores, I consider calcium as the preferable reducing metal.

II. Experiments With Nipissing Ore.

This was a small lot of rich ore which analyzed 9.65 percent cobalt, 4.65 percent nickel, 28.65 percent arsenic, 18.06 percent silver, 39 percent gangue. A second lot of ore analyzed 16.23 percent cobalt, 12.41 percent nickel, 34.21 percent arsenic, 4.31 percent silver.

The behavior of this ore was very similar to that of the smaltite ore above. When heated alone a splendid separation was obtained into crude silver (83 percent Ag), metal speiss and

slag. Upon cooling, the three layers can be very easily separated mechanically.[3]

The dividing line between silver and speiss is exceedingly sharp in the vacuum furnace product. We made a number of comparative runs in a carbon resistance furnace of the Moissan type, the gas pressure in the furnace being one atmosphere. Although a separation of the crude silver, speiss and slag was obtained, it was very incomplete and the volume of arsenic fumes evolved was most annoying.

In the vacuum furnace we found it convenient to make the runs in two stages. During the first stage the temperature was maintained at about 1250°-1350° for two hours. At the end of this time, instead of cooling down or tapping off the three components, the temperature was still further increased to 1550°-1600° and the charge kept there for about three hours. At this temperature the silver distilled out, leaving the speiss and slag behind.

The composition of the charge at the end of the first stage was, crude silver (lowest layer) 27 percent; speiss, 47 percent; slag, 20 percent, and arsenic (distillate) 8.5 percent. The addition of 5 to 10 percent of coke facilitates this separation of silver, speiss and slag. Its action is partly chemical, as a reducing agent, and partly physical, in so far as it keeps the charge porous, allowing the gases to escape readily. The crude silver of three runs assayed 81.34 percent, 82.21 percent and 83.7 percent silver. There was no silver found in the slag, and none in the distillate at the end of the first stage. At the end of the second stage (1600°) all of the silver was in the distillate and none in either speiss or slag.

Carbon and alumina crucibles were used. Should the gangue admixed with the ore be refractory, and its melting point be above or even near the melting point of silver, fluxes are preferably added. Their choice, of course, depends on the character of the gangue. The ore is preferably ground so as to pass through a forty-mesh sieve. In order to break up the speiss we proceeded as in the case of smaltite above. In run No. 376 we used 10 parts of calcium carbide, and 10 parts of calcium carbonate to 80 parts of ore. Only 1 to 2 percent of arsenic was

[3] U. S. Patent 1,013,931; Metall. Chem. Eng. **10**, 177 (1912).

left in the speiss after two hours heating at 1550°. Other additions, notably heavy spar ($BaSO_4$) chalcocite (Cu_2S) and silica (SiO_2) were tried, but results were not at all as favorable as those from the calcium carbide runs.

III. Antimony From Stibnite.

The cost of metallic antimony today is about six cents a pound. China produces about one-half of the antimony consumed in the world. The production of antimony metal in 1909 was: United States 3,278, China 7,937, France 5,444, Hungary, Italy and Japan, together, about 1,000 metric tons. The metal produced in the United States was derived largely from foreign ores. The American manufacturers have to compete with very cheap Chinese labor and in order that a metallurgical process meet with any success in this country it must be exceedingly simple and inexpensive.

In the English (Anderson's, Cookson's, etc.) process[4] the basic reaction is:

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS. \qquad (1.)$$

The ore is broken up and dropped into a fused bath of iron and iron sulphide.[5] The liberated antimony collects beneath the slag of sulphide of iron (rich in Sb) and is much contaminated with sulphur, arsenic, iron, copper, gold, silver, etc., necessitating subsequent refining. Notwithstanding its defects, the companies using the English process do very profitable work. They estimate their working costs, including loss (which is rather considerable) at from 200 s. to 250 s. per ton of pure regulus produced.

Another process is the so-called French, or volatilization process. The sulphide of antimony is volatilized in a shaft furnace and oxidized to Sb_2O_3. The oxide is caught in filter-bags, mixed with charcoal and soda, and heated on an open hearth. The reduction is effected with a reducing atmosphere in the furnace. The resulting regulus is quite pure, and is sold in the market as "French Star." The working costs amount to about 200 francs per ton of clean regulus produced from ore contain-

[4] Mineral Industry, 1906-1910.
[5] Mineral Industry, 1906, p. 47.

ing 50 percent antimony. To obtain a pure metal free from arsenic, etc., the "French Star" must undergo a further refining treatment.

A third process for the production of antimony has come into use within recent years, and consists in the electrolytic deposition of the metal from solutions of its sulphide plus sodium sulphide. This process is nowadays almost entirely confined to antimony ores rich in gold.[6]

All three of the processes mentioned are comparatively expensive and inefficient and are, for the most part, applicable only to rich ores (above 40 percent Sb) or concentrates. It seemed very promising that with the aid of the vacuum furnaces a distillation process could be worked out which would combine reduction and refining in one heating, thereby materially reducing the cost of production.

A point which presented itself very favorably at the outset is the low vacuum-boiling temperature of antimony. Under atmospheric pressure the metal melts at 632° (Pelabon) and does not boil until a temperature of 1500°-1700° is reached. The boiling-point in vacuum, however, is not more than a hundred degrees above the melting-point. Krafft[7] found that antimony boiled in quartz-glass tubes at 735°, the vapor pressure being "a few centimeters."

Our first experiments were made to determine whether it was possible to separate the metal from the sulphur by merely heating in vacuum without the addition of any reducing agent or other foreign material. We tried four different grades of ore:

Lot A analyzed 61.9 percent Sb; Lot B, 33.88 percent; Lot C, 50.16 percent; Lot D, 45.62 percent.

A sample of finely ground ore (Lot A) was heated in a graphite crucible at 750° for one-half hour, the vacuum being about 6 mm.

The result was that the sulphide distilled into the cooler parts of the furnace without any perceptible decomposition whatever. The possibility of decomposing the sulphide in this manner at a *lower* temperature, say 500° or 600° (melting-point of Sb_2S_3.

[6] Betts, Trans. Am. Electrochem. Soc. 8, 187 (1905); Electrochem. Ind. 3, 912 (1905).

[7] Berichte d. Ch. Ges. (1903), 36, 1704, 1712.

555°-Pelabon) appeared very slight, and consequently experiments were extended in other directions.

It appeared of interest to try the iron process in the vacuum furnace, in order to ascertain, among other things, whether the stability of the sulphide of iron was altered any under low pressure. A number of experiments were made with varied proportions of well-ground stibnite and iron, and at temperatures ranging from 600° to 1600°.

We obtained best grade metal and highest percentage output by the "iron method" when working according to the following proportions and conditions: Two parts of stibnite to one of iron, heated at 700° for 20 minutes and then at 1,200°—1,250° for one hour. We performed the heating in this manner, in two separate stages, for the reason that when we heated the charges directly up to the temperatures above 700°—800°, most of the sulphide of antimony would distill into the upper cooler parts of the furnace, without any decomposition whatever; on the other hand, whenever we heated the charge at 600°—700° for an hour or more and did not exceed this temperature, metallic antimony would be formed, but would all be either mechanically or chemically associated with the FeS, rendering a ready separation practically impossible. From our observations we have come to the conclusion that in the vacuum furnace at 600°—700° the reaction

$$Sb_2S_3 + 3\,Fe = 3\,FeS + 2\,Sb.$$

proceeds almost quantitatively in presence of an excess of iron. If this reaction is first allowed to take place, and the temperature then raised to 900°—1,250°, the antimony will readily be distilled away from sulphide of iron.[8] An attempt to shorten the duration of the second stage of the heating by employing higher temperatures failed since the sulphide of iron decomposed and partly volatilized at about 1,600°, resulting in a poor and contaminated output of antimony.

But keeping the temperature and conditions within the limits described above, the antimony metal obtained was always well crystallized (diameter of the crystals was about ¼ mm.) and of a very bright lustre. The output was practically quantitative,

[8] U. S. Patent 996,474; Metall. Chem. Engin. 9, 667.

only small amounts, about 3 percent of the total, either volatilized out of the crucible or were retained by the FeS.

The slag retained about 1 percent of the metal and 2 percent was lost by volatilization. This "iron method" is very simple and easily reproducible. It appears very convenient for the preparation of pure metal for therapeutic purposes such as for tartar emetic, sulphur auratum, etc., where the absence of the usual impurities, such as arsenic, copper and lead, is an absolute necessity. Our product was tested and found to be 99.98 percent pure. A detailed discussion of the comparative value of this method will be deferred until later.

One drawback of the English process in common use, and likewise of the iron process described above, is the use of iron as a reducing agent. Only when the prices for scrap iron are low and those of antimony regulus high, will it be profitable to obtain antimony by either process.

It seemed advisable to find a cheaper reducing agent, and we consequently made a number of experiments employing carbon (coke and charcoal) instead of iron. But the results were nowhere near as favorable as by the iron method. It was thought that carbon would more or less readily react with the sulphur to form carbon bisulphide:

$$2\ Sb_2S_3 + 3\ C = 3\ CS_2 + 4\ Sb \qquad (2)$$

and the charges were made upon the basis of this theory, using a slight excess of carbon. The product was hard to obtain in the crystalline form and was generally highly contaminated with sulphide (Runs Nos. 145, 150, 153, 157, 161, 163). The percentage output was comparatively low (best about 80 percent), in spite of protracted heatings. We were led to conclude that the temperature at which CS_2 will be readily formed from Sb_2S_3 and C in a vacuum lies above the boiling-point of Sb_2S_3.

The heat of formation of CS_2 is 26 calories,[9] whereas the heat of formation of Sb_2S_3 is 38.2 calories,[10] per gram molecule.

The third and last method of reduction we applied to the stibnite was the one that had given us good results with other ores. It is based on the reaction:

[9] Thomsen, Ber. d. Chem. Gesell., **16**, 2616 (1883).
[10] Guinchant and Chrétien, Compt. rend., **139**, 51 (1904).

$$Sb_2S_3 + 3\,CaCO_3 + 6\,C = 3\,CaS + 9\,CO + 2\,Sb$$

That is to say, instead of using carbon alone, as in the second method, we used a mixture of carbon and ordinary powdered limestone. Brown[11] had used a modification of this method when reducing stibnite in an ordinary electric furnace. He employed lime instead of the carbonate, and although the difference between his and our method at first appears very slight, it seems comparatively important when we begin to consider that the liberated CO_2 and CO (CO_2+C) not only assist the extraction and distillation of Sb mechanically by keeping the slag porous, but the CO also furthers the reduction process. Brown had worked in open and closed crucibles, but the output was poor and the loss of metal very considerable. Brown's experiments showed "that the reduction and distillation of antimony (under *atmospheric* pressure) is incomplete, even when the mixture is heated in an electric furnace to a very high temperature." As was stated in the introduction, one great advantage in the use of the vacuum over the ordinary electric furnace lies in the considerably lower boiling-point of the metal under low pressure. We obtained best results under the following conditions: for every 11.3 parts of stibnite (62 percent Sb), 12 parts limestone, 2½ parts coke and 6 parts fluorspar (Runs No. 189 to 203).

All ingredients of the charge were finely ground (40 mesh) and thoroughly mixed. The heating was performed in two stages; the temperature was gradually raised to 600°—700°, and maintained at that point for one to one and a half hours, until the following reaction was practically complete:

$$Sb_2S_3 + 3\,CaCO_3 + 6C = 2\,Sb + 3\,CaS + 9\,CO \quad (3)$$

Thereupon the current was slowly increased until a temperature of about 1,300° was obtained, and after about one hour's heating at this point the charge was allowed to cool in vacuum. The addition of CaF_2 to the charge seems to facilitate the separation (by distillation) of the Sb from the slag in the second stage of the heating.[12] At all events, we have obtained better results with than without the addition of this flux. The slag

[11] Trans. Am. Electrochem. Soc. 9, 113 (1906).
[12] U. S. Patent 996,474; Metall. Chem. Eng. 9, 667.

was one solid mass, with carbon particles evenly distributed throughout. It was analyzed for Sb, and only very small quantities were found. The distilled Sb was very bright and lustrous. It analyzed 99.95 percent Sb. This method was tried out on the several lots of ore enumerated above and found to work equally well for all.

We have used equation (3) as the basis of our charge proportions.

That the reaction does actually proceed mainly according to the equation (3) and not according to the equation given by Brown:

$$2Sb_2S_3 + CaCO_3 + 7C = CaC_2 + 3CO + 3CS_2 + 4Sb$$

seemed evident from the fact that our experiments with stibnite and carbon alone did not readily yield CS_2 under the conditions of temperature and pressure employed and that furthermore we could prove the presence of large quantities of CaS in the slags and but very little carbide. The carbon merely reacts with the CO_2 liberated by the limestone to form CO and very probably the latter, as mentioned above, greatly assists in the reduction of the ore.

Conclusion.

The $C + CaCO_3$, or calcium carbide-vacuum method above described, is cheap, and when the conditions are properly chosen the output is over 95 percent. The product is practically equal in quality to that obtained by the "iron method." The calcium carbide method is cheaper than the English process employing iron as reducing agent.

It also appears to be cheaper than the French process, in so far as it does away with the two or three separate heatings—concentration, volatilization, oxidation and reduction—combining all three in one. Furthermore, the heating in the vacuum furnace proceeds at a comparatively low temperature, and all loss of metal due to "burning" and oxidation is avoided. Another advantage of the vacuum processes is the greater speed of the reactions, due to the fact that the gaseous products are readily removed.

This same vacuum process, with slight modifications, can be

made to apply equally well to the anode slime from the electrolytic refineries. Our lot of slime contained about 35 percent antimony, 5 percent copper, 10 percent lead, 8 percent bismuth, 8 percent arsenic, 15 percent silver and 0.15 percent gold.

In the chapters above, I have outlined vacuum furnace processes which seem to be applicable to a large variety of ores. We have applied the same general principle to ores of nickel, copper, zinc, manganese, and silver (tetrahedrite) and although the tests on these ores were more of a qualitative nature, the results were such as to encourage further research.

I should like to add in this connection that Mr. W. C. Arsem of our laboratories has worked out a very neat process for separating gold and silver, which consists in heating the alloy of these two metals in the vacuum furnace to a temperature of about 1,300°, to distill off the silver. If platinum is present in the alloy, the temperature is raised, after the silver distillation is complete, to about 1,500°, and the gold distilled over.[13]

This work was carried out at the General Electric Research Laboratories at Schenectady and at Harrison. I am very much indebted to Dr. W. R. Whitney for many valuable suggestions during the course of the research and to Messrs. W. E. Ruder and L. B. Schleeder for their admirable assistance in carrying out the experiments.

Harrison Development Laboratories,
General Electric Company,
March 22, 1912.

DISCUSSION.

PROF. JOS. W. RICHARDS: In connection with the distilling of arsenic away from a Cobalt type of ore, I have done a good deal of work myself in blow-pipe analyses, distilling off arsenic in the reducing flame on charcoal under the blow-pipe, and under these conditions, in an atmosphere of CO and CO_2 and nitrogen, there is expelled, quantitatively, three-quarters of the arsenic. I do not understand why we should not get that much, or more, of

[13] U. S. Pat. 998,665.

the arsenic expelled in a vacuum. The reaction of the substances present are as follows: The cobalt arsenide becomes Co_2As, losing three out of four atoms of arsenic, and leaving a definite compound which you can reproduce definitely under those conditions. As to the volatilization of silver before the blow-pipe, I have frequently taken an alloy of gold and silver, in the atmosphere just before the point of the blowpipe flame, and volatilized most of the silver, leaving the gold behind. You cannot get the last of the silver out, but it volatilizes down to 5 percent silver and 95 per cent. gold. In the electric furnace it has been proposed to separate silver from gold in that way.

Dr. C. G. Fink: As regards the cobalt-arsenic compound, we do break it up quite completely in the presence of calcium carbide.

If the ores are very rich in arsenic and omitting the calcium carbide, we can get out considerable quantities of arsenic, but with the same weight of metal (Co, Ni, Fe) to start with, we always get down to the same compound no matter how much arsenic there is to begin with. For all practical purposes, it is better to add calcium carbide, since the separation is more complete.

The reactions that take place under atmospheric pressure in the presence of air are not altogether comparable with those taking place in a vacuum. Ores of the smaltite, cobaltite and mispickel type are decidedly more stable in vacuum than when roasted in the air. By the addition of calcium carbide, however, the arsenic and sulpho-arsenides are broken up in the vacuum furnace, and the loss of precious metals is reduced to a minimum.

Dr. Carl Hering: Although I have no doubt there is a good reason, I do not quite see why the vacuum furnace should be so advantageous for arsenic ore, since arsenic is so easily expelled at atmospheric pressure. It is going to extra trouble to use the vacuum furnace, and atmospheric pressures have been successfully used for arsenic. The arsenic separates very easily and satisfactorily from some ores at atmospheric pressures, as I know from experience.

Dr. Fink: The ores found at Cobalt are very rich in silver, and to expel the arsenic under atmospheric pressure would entail

considerable loss in silver. The mining companies do not get anything for the arsenic or for the other by-products. They sell the ore for the silver content only, because all the processes now used are so cumbersome and inefficient, that it costs more to get out the cobalt than it is worth. What is wanted is a simple, cheap method for the extraction of the silver and the separation of the arsenic from the cobalt and nickel.

Dr. Richards: The difficulty of removing all the arsenic by roasting, in the presence of silver, is due to the formation of the undecomposable silver arsenate. You can roast it as carefully and as long as you please, but in the presence of a large amount of silver you have a considerable amount of arsenic left in an undecomposable form, and that causes the formation of silver arsenide subsequently, in the smelting of the roasted ore.

Mr. W. McA. Johnson: Looking at the process from a commercial standpoint, I will say that one cannot sell the cobalt for any price that is worth while, or the oxide of arsenic at any price that is worth while. I believe they are selling for $1.75 per 100 pounds. It strikes me, that if you are going into a business like that, you will have to hire about twenty-five experimenters and salesmen to develop new uses and markets for the cobalt oxide and oxide of arsenic. There is several years' supply of the oxide of cobalt on hand at the present time.

Mr. Johnson (*Communicated*): Continuing the line of my previous remarks, I would point out the possibility of increasing the demand for cobalt oxide and arsenious oxide by developing new uses for them. The potential demand for any new material is great, as civilization grows and expands. If new ores were found, a new process to recover the by-product values of "cobalt" ores would arise; or, conversely, if a new process should produce these and sell them at a low price, this low price would stimulate chemists and the public to find new uses. The two are interdependent: New demands would make a new process, and a new process would make new demands.

About three years ago I did considerable work on treating "cobalt" ores either directly by chlorin gas, or by treating speiss, made in a cupola furnace or electric furnace, by chlorin gas. The process, tho practical, was not commercial because the market

for our by-products was restricted. What experience I have had both in commercial and experimental work on nickel-cobalt ores inclines me to believe that this is the most practical way to treat these ores. Economic geologists are of the opinion that the cobalt field will last for a long time, but that the cost of finding the ore will increase. It is thus imperative to have some neat and cheap process to extract the values, and to have new uses for these commercially new products, in order to compensate for increased mining costs. It is interesting to note that the demand for arsenious oxide has risen greatly in the past few months, and the price is now about $3.50 per 100 lb., or double the price which has prevailed for two or three years past.

Dr. Fink: I should like to refer Mr. W. McA. Johnson to a recent paper by F. J. G. Beltzer on a chlorination process applied to the "cobalt" ores.[1] Owing to the many steps involved, I do not believe a process of this type to be as cheap as the vacuum process. As regards new applications for cobalt, the alloys of this metal with gold, chromium[2], copper, tungsten, and molybdenum, are most interesting.

Copper-cobalt alloys are soft and easily wrought. By oxidizing the surfaces of these alloys, very artistic effects can be brought about.

[1] Mon. Sci., **13**, 633.
[2] J. Ind. Eng. Chem., **2**, 397.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

THE BOLTWOOD STANDARD OF RADIOACTIVITY.[1]

By Merle Randall.

As late as 1903 we find that Strutt,[2] in his study of the radioactivity of ordinary materials, used as a standard, the activity of a "crystal of uranyl nitrate four by twelve millimeters." Allan[3] studied the activity of freshly fallen snow, and took as his standard the activity of a given weight of uranium, in uranium oxide.

Elster and Geitel[4] studied the radioactivity of clay and spring sediment. They took for comparison the activity of uranyl-potassium sulphate. Blanc[5] used as a standard an equal weight of uranium nitrate.

McCoy[6] has proposed to use as a standard of activity the ionization produced between parallel plates by the *alpha* rays from one square centimeter of urano-uranic oxide[7] of sufficient thickness to give the maximum *alpha*-ray activity. McCoy has shown[8] that this standard is reproducible with a high degree of accuracy.

Boltwood[9] has used the ionization of thin films of urano-uranic oxide which had a negligible amount of *alpha*-rays absorbed by the film itself, as a standard.

The ratio of radium to uranium in an old natural mineral is a constant,[10] independently determined by Boltwood, McCoy, Ross

[1] Abstract of a thesis presented to the Faculty of the University of Missouri in partial fulfillment of the requirements for the degree of Master of Arts, June 1909.

[2] Strutt, R. J., Phil. Mag. **5**, 680 (1903); Nature **67**, 369 (1903).

[3] Allan, S. J., Physic. Rev., **16**, 237, 306 (1903).

[4] Elster and Geitel, Physik. Z. **5**, 321 (1904).

[5] Blanc, G. A., Phil. Mag., **9**, 148 (1905).

[6] McCoy, H. N., Ber. d. Chem. Gesell., **37**, 2641 (1904); Physic. Rev., **20**, 381 (1905); J. Am. Chem. Soc., **27**, 391 (1905); Phil. Mag., **9**, 176 (1906).
Goettsch, H. M., Thesis, University of Chicago. The Absorption Coefficients of Uranium Compounds.
Mc Coy and Ross, J. Am. Chem. Soc., **29**, 1698 (1907).

[7] McCoy and Ashman, Am. Jour. Sci., **26**, 528 (1908).

[8] McCoy, *loc. cit.*

[9] Boltwood, B. B., Am. Jour. Sci. **21**, 409 (1908).

[10] Boltwood, B. B., Am. Jour. Sci. **18**, 97 (1904); Nature, **70**, 80 (1904); Phil. Mag. **9**, 509 (1905).
Rutherford and Boltwood, Am. Jour. Sci., **20**, 56 (1905); **22**, 1 (1906).
McCoy, H. N., Phil. Mag., **11**, 176 (1906).
McCoy and Ross, Physic. Rev., **24**, 124 (1907).
Boltwood, B. B., Am. Jour. Sci., **25**, 259 (1908).

and others. Boltwood has suggested that the quantity of radium emanation associated with one gram of uranium in an old natural mineral, such as pitchblende, be used as a standard of radioactivity.[11] This method has since been used by a large number of other investigators.[12] As only a part of the equilibrium quantity of the radium emanation is retained by the mineral,[13] the quantity of emanation lost must either be determined and corrected for, or a solution of the mineral must be stored for a definite time. The various methods of using this emanation standard will be described below.

The compounds of radium have also been used as standards of activity. The purity of radium chloride or radium bromide can be ascertained by measuring the heat given off spontaneously by a known weight of radium preparation in equilibrium with its products.[14] This standard has been used extensively by Curie and others,[15] and while it is probably the most satisfactory it is, nevertheless, not generally available on account of the high cost of radium preparations and of the difficulty of ascertaining the purity of a given specimen.

The Röntgen Society has proposed[16] that one milligram of pure radium bromide be taken as the standard of radioactivity, and that the ionization due to the *gamma*-rays, after passing through one centimeter of lead, be taken as the measure.

The conductivity of gases has been extensively studied,[17] the conductivity of the air being used as a standard. It has been shown[18] by Elster and Geitel and others that the normal conductivity of air varies at various times during the day, and

[11] Boltwood, B. B., Am. Jour. Sci., **18**, 381 (1904); Phil. Mag. **9**, 599 (1905).
[12] Strutt, R. J., Proc. Roy Soc. **78**, 151.
Joly, J., Phil. Mag. [6] **15**, 385 (1908); Radioactivity and Geology. Constable. London, 1909.
Fletcher, Arnold L., Phil. Mag. **20**, 36 (1910), **21**, 102, 770 (1911).
[13] Boltwood, B. B., Phil. Mag., **9**, 599 (1905).
Strutt, R. J., Proc. Roy. Soc., **77**, 472 (1906).
[14] Rutherford and Barnes, Phil. Mag., **8**, 202 (1904).
[15] Curie and Laborde, Comptes rendus, **138**, 1150 (1904).
Eve and McIntosh, Phil. Mag., **14**, 231 (1907).
[16] Röntgen Ray Society. Nature, **77**, 543 (1908). Journal Röntgen Ray Soc., Feb. 1908.
[17] Strutt, R. J., Proc. Royal Soc., **68**, 126 (1901).
Thomson, J. J., Proc. Camb. Phil. Soc., **11**, 505 (1902).
Börnstein, R., Ber. Physik. Ges., **22**, 404 (1903).
Bumstead and Wheeler, Am. Jour. Sci., **16**, 328 (1903).
Himstedt, F., Ann. Physik., **13**, 573 (1904); Ber. d. Naturf. Gesell. Frieburg, **14**, 181 (1904).
Blanc, G. A., British Association Reports, Camb., 71 (1904).
[18] Elster and Geitel, Ann. Physik., **2**, 425 (1900); Physik. Z. **2**, 560 (1901).
Saake, W., Physik. Z., **4**, 626 (1903).
Wood and Campbell, Phil. Mag., **13**, 265 (1907).

from place to place, so that the air standard is at once excluded in any series of measurements where accuracy is required.

The activity of many spring waters and other ordinary materials[19] has been expressed in terms of volts fall of potential of a charged body per hour, without data regarding the electrostatic capacity of the body, or the size of the vessel in which the ionization took place. Since the rate of fall of potential of a charged body is inversely proportional to the electrostatic capacity of the system, for a constant ionization,[20] this system of expressing the results of radioactive measurements cannot be used when comparative results are desired.

Numerous results on the radioactivity of water samples, gases and other ordinary materials[21] have been expressed in the C. G. S. electrostatic units. In some cases the size and shape of the testing vessel were given, and in others not. This method of expressing the activities was first employed by Gerdien, then by Mache, and Curie and Laborde, and later by Engler and others.[22] This method is very generally employed on the continent of Europe for expressing the activity of the air, water samples, minerals, etc.

It is very desirable that the results expressed in terms of some one of the above standards of radioactivity should be convertible into the terms of any other standard.[23] A great many measurements have been made upon the activity of spring waters, minerals, rocks and other common materials, but in general no comparison of the results of one investigator with those of another has or can be made. Of the above standards, only three are at the present time generally available, *i. e.*, the McCoy

[19] Himstedt, F., Ann. Physik., **12**, 107 (1903); Ber. d. Naturf. Gesell. Freiburg, **13**, 101 (1903).
Rausch, H. F., Physik. Z., **5**, 130 (1904).
Costanzo and Negro, Physik. Z., **7**, 350 (1906).
Hayek, H. V., Z. d. Ferdinandeums für Tyrol u. Vorarlberg, **50**, 524 (1907).

[20] Rutherford, E., Radioactivity, 2nd Edition, Camb. Press., 100 (1905).

[21] Gerdien, H., Physik. Z., **4**, 632 (1903). Mache, H., Wien. Ber., **113**, 1329 (1904).
Curie and Laborde, Comptes rendus, **138**, 1150 (1904).
Engler and Sieveking, Z. anorg. Chem., **53**, 1 (1904).
Campbell, N. R., Proc. Camb. Phil. Soc., **13**, 132 (1905); Phil. Mag., **11**, 217 (1906).
Mache and Travis Rimmer, Physik. Z., **7**, 617 (1906). Radium **3**, 289 (1906).
Sury, Jos., Mitt. Naturf. Gessell. Freiburg Chem., II, **1**, 78 (1906); Chem. Zentral. I, 1282 (1907).
Koch. K. R., Physick. Z., **7**, 806 (1906); Ber. Physik. Ges., **8**, 846 (1906).
Henrick, Ferd., Physik. Z., **8**, 112 (1907).
Ebler, E., Z. angew. Chem., **21**, 737 (1908).

[22] *Loc. cit.*

[23] McCoy, H. N., Phil. Mag., **11**, 176 (1906).
McCoy and Ross, J. Am. Chem. Soc., **29**, 1698 (1907).

urano-uranic oxide standard, the Boltwood emanation standard and the C. G. S. absolute standard. McCoy and Ross have recently studied the relation between the McCoy standard and the C. G. S. electrostatic standard. They found the ionization current due to the *alpha*-rays from a thick film of urano-uranic oxide was 5.79×10^{-13} amp., or 1.737×10^{-3} C. G. S. electrostatic units, per square centimeter. The specific activity of uranium, defined as the total ionization current from one gram of uranium when all the radiation is absorbed in the air, is 796 McCoy units.[24] The total ionization current from one gram of uranium free from its products is then 4.61×10^{-10} amperes or 1.38 C. G. S. electrostatic units.

Boltwood has shown[25] that if the activity of uranium, free from its products, be taken as 1.00 for his electroscope, that the activity of the radium emanation in equilibrium is 0.62, that of the radium *A* is 0.54, that of the radium *B* is 0.04, and that of the radium *C* is 0.91, or a total of 2.11 times as active as the uranium with which they are in equilibrium. Now, if the equilibrium quantity of radium emanation from one gram of uranium was introduced into an electroscope, and the equilibrium amount of radium *A*, radium *B* and radium *C* allowed to accumulate, the activity would be $4.61 \times 10^{-10} \times 2.11$ or 9.73×10^{-10} amperes, or 2.92 C. G. S. electrostatic units, if all the *alpha* particles had the maximum range in air.

In none of the forms of electroscopes in use do all the *alpha* particles have their maximum range in air. At least one-half of the radiation from the radium *A*, radium *B* and radium *C* is absorbed by the walls, since these products are deposited upon the walls and radiate equally in all directions. The emanation is distributed thruout the space of the ionization chamber, but some of the *alpha* particles will not have their maximum range. We may take, then, for the ordinary electroscope, as the maximum limiting activity for the emanation 0.62, for the radium *A* 0.27, radium *B* 0.02 and radium *C* 0.46, or a total of 1.37 times the activity of uranium. The ionization current is ordinarily measured about 3 hours after the emanation has been introduced into the electroscopes. During this interval the activity of the emanation

[24] Rutherford, E., C. R. International Cong. Radiologie, Bruxelles (1910), **1**, p. 362.
[25] *Loc. cit.*

(with which the induced activity is in equilibrium) has decreased to 97.8 percent[26] of its former value. Hence we have for the theoretical maximum ionization current 1.34 times that produced by 1 gram of uranium or 6.18×10^{-10} amperes. The current per gram of radium[27] is 2.1×10^{-3} amperes.

As has been pointed out above, the investigators on the continent of Europe have used the C. G. S. electrostatic standard, while those in England and this country have generally used the Boltwood radium-emanation standard, in expressing the activity of such materials as water, gases, rocks and other common materials. McCoy and Ashman have already[28] determined the relation between their standard, the Boltwood uranium oxide standard and the C. G. S. electrostatic standard. I have calculated above the theoretical relation which should exist between the Boltwood radium-emanation standard and the C. G. S. electrostatic standard.

At the suggestion of Prof. Schlundt this relation between the Boltwood emanation standard and the C. G. S. electrostatic standard has been studied experimentally, using several forms of electroscopes. Definite quantities of radium emanation were separated from solution by several of the prevailing methods, and introduced into calibrated electroscopes. From the rate of leak and the electrostatic capacity of the electroscope the current in amperes and in C. G. S. units was calculated.

Standard Samples of Radium Emanation: The uranium mineral used as a source of radium emanation was a uraninite of unknown origin, purchased from the firm of Eimer & Amend.

The analytical determination of the uranium in the sample of standard uraninite was conducted by a modification of the method described by Boltwood.[29] Mean of the three determinations on the air-dry uraninite, ground to pass a sieve 120 meshes per inch (48 per cm.), 53.03 percent uranium (calculated on the assump-

[26] Calculated from the equation $I = I_0 e^{-\lambda t}$ in which I_0 is the initial activity, e the base of natural logarithms, and t the time in seconds. The value of λ was taken as 2.085×10^{-6}. (Curie, Traité de Radioactivite (1910) II, p. 536).

[27] The quantity of radium emanation in equilibrium with 1 gm. of radium has been called the "Curie."

[28] *Loc. cit.*

[29] Boltwood, B. B., Phil. Mag., 9, 603 (1905). The uranium phosphate was precipitated in the presence of ammonium acetate. See Brearley, H., Analytical Chemistry of Uranium, Longmans, Green and Co., p. 10.

tion that the green salt weighed contained 68.55 percent of uranium,[30] an assumption which has been verified by Boltwood).[31]

It is well known that the moisture content of finely powdered minerals changes materially. In order to have a check on the moisture content of the powdered uraninite, two samples were weighed out into platinum crucibles, placed in a steam oven, and allowed to remain two hours. Two determinations gave a mean loss, by heating two hours at 100° C., of 0.80 percent.

The percentage of uranium in the mineral, when referred to the finely powdered material heated two hours at 100° C., was 53.46.

This sample of uraninite, carefully standardized gravimetrically, was used in the preparation of the five stock solutions of definite content[32] of uranium. These stock solutions were made acid by adding hydrochloric acid, and samples taken, when stored, gave solutions of known radium emanation content.

Samples of material containing radium salts in solution are generally stored in a flask fitted with a tightly fitting rubber stopper.[33] When the emanation is to be boiled off, the stopper is removed and the flask attached to the collecting apparatus very quickly, in order to avoid, as much as possible, loss of the radium emanation.

Schlundt and Moore[34] have studied the loss of radium emanation from mineral waters. They found that the quantity of radium emanation lost by these solutions of very small content of emanation, when heated to 95° C., was thirteen percent. The concentration of radium emanation in the solutions to be studied was much greater than in the above experiments, and it was desired to avoid any loss which might possibly occur during the change of stoppers.

The storage flasks (Figs. 1 and 2) consisted of a 200 c.c. Erlenmeyer flask *A* fitted with a one-holed rubber stopper and closed by means of a screw clip *E*. This design of storage flask proved very convenient for attaching to the various forms of apparatus for separating the radium emanation which are

[30] Brearley, H., *Loc. cit.*
[31] Boltwood, B. B., *Loc. cit.*
[32] Eve, A. S., Am. Jour. Sci., **22**, 4 (1906). Phil. Mag., **18**, 102 (1909).
[33] Schlundt and Moore, J. Physic. Chem., **9**, 320 (1905).
Strutt, R. J., Proc. Royal Soc., **77**, 472 (1906).
[34] Schlundt and Moore, J. Physic. Chem., **9**, 320 (1905).

described below, and entirely obviated any loss of the emanation due to the change of stoppers as in the former arrangements.[35]

Eleven series of samples, eighty in all, containing from 0.001 gram to 0.3 gram uranium, were prepared from the standard stock solutions in the manner described. The quantity of radium emanation in equilibrium with radium attains its maximum value after the lapse of about a month.[36] The samples were all stored over six weeks before they were boiled off, so that the quantity of radium emanation reached the maximum.

APPARATUS FOR BOILING OFF THE RADIUM EMANATION.

Inasmuch as a number of different forms of apparatus have been devised and used by different investigators for separating radium from solutions of radium salts, it seemed desirable to study the relative efficiency of the more common forms. In all, five types of apparatus were used, and these will now be described in the order of their adoption during the progress of the investigation.

The Strutt Apparatus: In the original Strutt apparatus[37] it is possible that some of the emanation contained in the receiver will not be introduced into the electroscope on account of the trapping of some of the gas in the connecting tubes. Also the operation of discontinuing boiling is rather difficult. The original design was slightly changed so as to avoid trapping any gas in the connecting tubes, and also to simplify the manipulation connected with the stoppage of the boiling. The improved apparatus is shown in Fig. 1.

The storage flask *A* containing the stored solution was attached to the reflux condenser *F*. The three-way stop-cock *G* was so arranged that in the first position of the stop-cock the receiver *I* could connect with the condenser *F;* by a quarter turn it would cut off the receiver *I* and connect the condenser *F* with the air through *H;* by another quarter turn the whole apparatus could be placed in communication with the outside air. The receiver *I* was connected with the leveling bulb *J* by means of a rubber tube which could be closed by means of the screw clip *L*. Com-

[35] The samples prepared from solution *D*, which were boiled off in the Boltwood apparatus (Fig. 3) were stored in flasks fitted with two glass tubes closed by the one large screw clip *E*.

[36] Rutherford, E., Radioactivity, 2d Edition, p. 372.

[37] Strutt, R. J., Proc. Royal Soc., **77**, 472 (1906).

munication with the electroscope was made through the side tube *M* and the glass-stoppered U-tube *N* containing concentrated sulphuric acid and glass wool.

The manipulation was as follows: The stop-cock *G* was turned to the first position. The receiver *I* and the leveling bulb *J* were filled with distilled water and the level adjusted so that the water filled the receiver to the lower edge of the branch tube *M*. The screw clip *L* and the stop-cock *P* were then closed. The screw clip *L* was now opened and the leveling bulb *J* lowered in order to test for possible leaks. If the apparatus was tight the screw clip *E* was opened. A slow current of water was kept running through the jacket of the condenser *F*. The contents

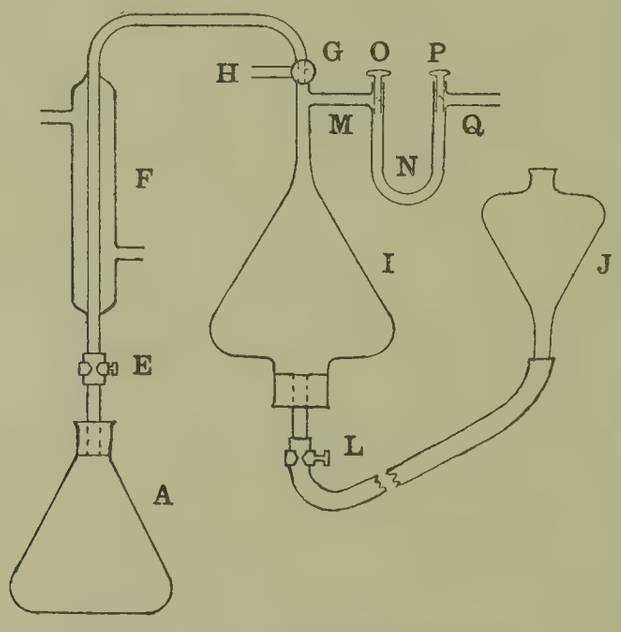


Fig. 1. The Strutt Apparatus.

of the flask *A* were heated to boiling and kept in rapid ebullition for at least twenty minutes, when the water was turned off, and that in the jacket of the condenser allowed to run out. After the steam had swept all the gases in the condenser over into the conical receiver *I*, the cock *G* was turned to the second position, or so that the receiver *I* was cut off, and the flask *A* placed in communication with the outside air, after which the boiling was discontinued. The operation up to this point results in separating the emanation accumulated in the solution in the flask *A* and storing it in the receiver *I*.

In order to avoid the introduction into the electroscope of thorium emanation and its disintegration products, the gas was

stored in the receiver *I* for at least twenty minutes before it was introduced into the electroscope.

In order to transfer the emanation now stored in the receiver *I* into an electroscope, the latter was partially exhausted by means of water suction. The exhausted electroscope was now connected to the U-tube *N* by means of a piece of heavy rubber tubing. As an extra precaution, to avoid any sulphuric acid being carried over into the electroscope, a plug of cotton was placed in the side tube at *Q*. The brass stop-cock of the electroscope was

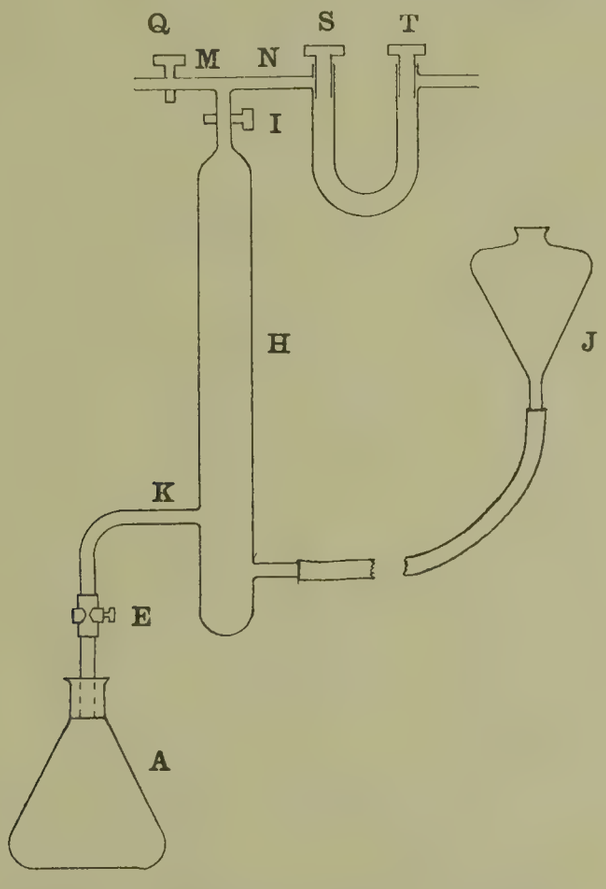


Fig. 2. Schlundt and Moore Apparatus.

opened, then the stop-cock *P* of the U-tube very slowly, so that about five bubbles per second passed through the sulphuric acid. When the level of the water in the receiver *I* reached the lower edge of the side tube *M*, the screw clip *L* was closed and the three-way stop-cock *G* turned to the third position, so that the whole apparatus was connected with the outside air. After the connecting tubes had been swept free of the emanation by means of the current of air, and the pressure in the electroscope had risen to nearly that of the atmosphere, the stop-cock of the electroscope was closed and the U-tube disconnected. Finally

the pressure in the interior of the electroscope was equalized with that of the atmosphere by opening the stop-cock, after which it was closed.

Schlundt and Moore Apparatus: The second form of apparatus was essentially that described by Schlundt and Moore.[38] It consisted of a gas burette *H* (Fig. 2), provided with a stop-cock *I* and a leveling bulb *J*. The storage flask *A* was attached to the branch tube *K*. This is the apparatus essentially as described,[39] but the introduction of the emanation without trapping some of it in the connecting tubes was rather difficult. The apparatus

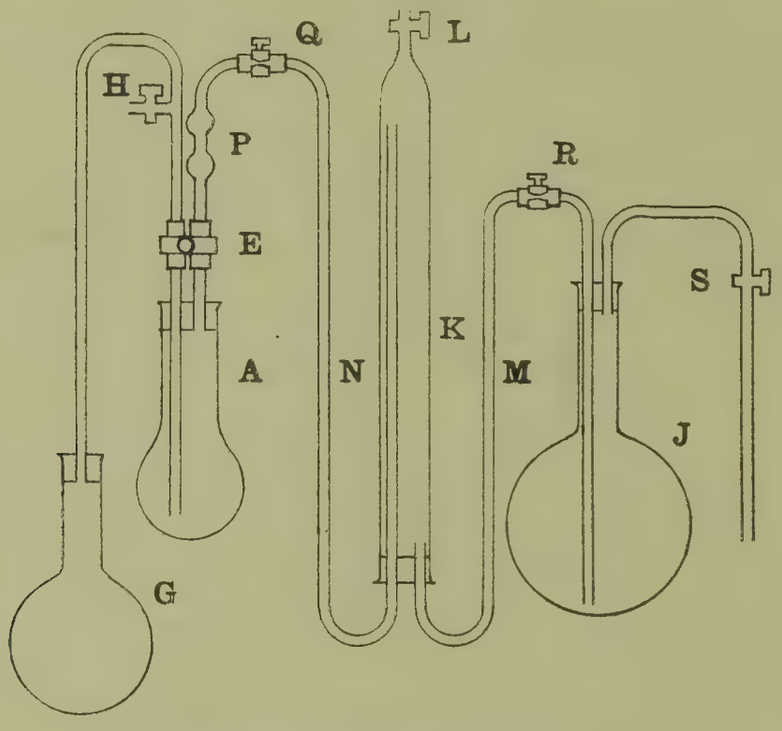


Fig. 3. Boltwood Apparatus.

was therefore modified with a view to obviating this difficulty. A T-tube *MN* with stop-cock *Q* was sealed on just above the stop-cock *I*. To *N* was sealed a glass-stoppered U-tube containing concentrated sulphuric acid and a plug of glass wool.

The manipulation of this apparatus was comparatively simple, but required close attention. After connecting the storage flask *A* to the side tube *K* of the burette, the screw clip *E* was opened and the solution in the flask *A* boiled from twenty to thirty minutes. At intervals during the boiling the flame was withdrawn and the water from the burette allowed to fill the flask.

[38] Schlundt and Moore, J. Physic. Chem., 9, 320 (1905).
[39] Schlundt and Moore, *Loc. cit.*

In this way the greater part of the water through which the emanation had bubbled was boiled. This operation minimized the loss of emanation by absorption in the water in the burette *H*.

The separated gases were allowed to stand in the burette for at least twenty minutes, and transferred to the electroscopes. When the level of the water in the burette reached the level of the branch of the T-tube, the stop-cock *I* was closed and the stop-cock *Q* opened so that a slow current of air would sweep any gas in the connecting tube over into the electroscope.

Schlundt and Moore Apparatus for Water Samples: This was the apparatus used by Schlundt and Moore for the separation of radium emanation from solutions of large volumes,[40] such as water samples. A drying train *QMNST* (Fig. 2), described in connection with the previous apparatus, was used in order to facilitate the transfer of the gas to the electroscope.

The Boltwood Apparatus: The Boltwood apparatus used (Fig. 3) was essentially that described by Boltwood[41] for the collection of the radium emanation occluded in minerals. The samples to be boiled off in this form of apparatus were stored in a slightly different form of storage flask.

The McCoy Apparatus: This form of apparatus was not studied extensively. It was used as described.[42]

Another form of apparatus for separating radium emanation from its aqueous solutions should be mentioned. It was designed and used by Soddy and Mackenzie for the accurate estimation of small quantities of radium emanation contained in minerals. The emanation was removed from the solution of the mineral to be tested by boiling in vacuo. The gases were passed through phosphorus pentoxide and collected over mercury. The gases were then expelled into an electroscope.[43] This method is probably the most accurate for separating the emanation, but the necessary apparatus was not available for these experiments.

Besides studying the separation of radium emanation from aqueous solutions, some experiments were conducted to determine the quantity of radium emanation occluded in the standard

[40] Schlundt and Moore, J. Physic. Chem., **9**, 320 (1905).
[41] Boltwood, B. B., Am. Jour. Sci., **18**, 380 (1904); Nature, **70**, 80 (1904); Phil. Mag., **9**, 599 (1905).
[42] McCoy and Ross, J. Am. Chem. Soc. **29**, 1700 (1900).
[43] Soddy and Mackenzie, Phil. Mag., **14**, 272 (1907).

uraninite. The apparatus used was that described by Boltwood,[44] and used by Schlundt and Moore[45] in standardizing their electroscopes.

THE ELECTROSCOPES.

Electroscope No. 2: This electroscope was essentially the Boltwood modification of the C. R. T. Wilson electroscope.[46] It consisted of a rectangular brass frame 15 x 10 x 5 cm. (Fig. 4). Small strips of brass 3 mm. x 3 mm. were soldered on the inside of the frame, 4 mm. from the edges. Two pieces of plate glass

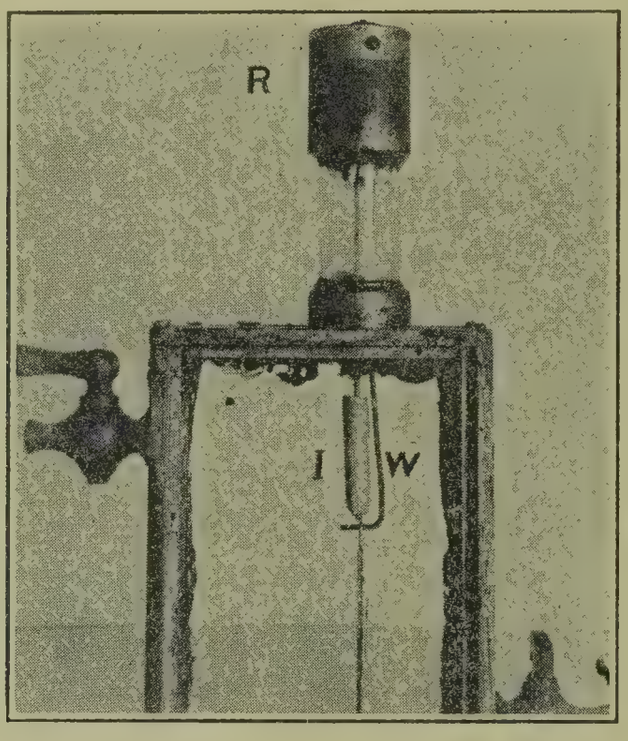


Fig. 4. Electroscope No. 2.

6 mm. thick were mounted in the recesses thus formed on the front and back of the frame.

The method of mounting these glass plates so as to make air-tight joints is of particular importance. Boltwood[47] used hot sealing-wax; marine glue and picein[48] have been used in this laboratory to some extent, but all of these have presented some difficulty in securing perfectly air-tight joints. The following method of procedure was found to give uniformly satisfactory

[44] Boltwood, B. B., *Loc. Cit.*
[45] Schlundt and Moore, *Loc. Cit.*
[46] Boltwood, B. B., *Loc. Cit.*
[47] Boltwood, B. B., *Loc. Cit.*
[48] Walter, B., Ann. Physik., 18, 860 (1905).

results. The surfaces of the metal and of the glass were first thoroughly cleaned. The picein was warmed just enough to make it soft and easy to work into shape with a knife or spatula. The wax was then pressed tightly into the groove with a knife. Both glasses were now placed on the bed of picein and the whole firmly pressed together. The glass plates should fit the frame closely, or the picein joint will not hold tight in warm rooms or in hot weather. The frame, with the glasses in position, was placed, front down, on top of a steam oven or over a radiator, and weighted to press the plates home. The frame was

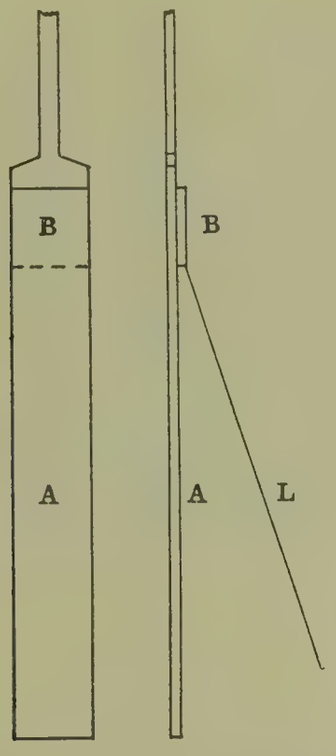


Fig. 5. Detail of Leaf System.

left on the radiator until the wax had softened thoroughly and the plates had sunk as close together as possible. The frame was now transferred to a table, front down, and the weights replaced. The whole was allowed to stand in this position for three or four hours. In this way the wax fills all the space between the glass and frame with a thin film, which adheres very firmly.

The glass tube and cap *R* are objectionable features of this form of electroscope, as they have a tendency to change position, due to the softening of the wax, when placed in a warm room.

The leaf system, insulated by means of the sulphur rod *I*, Fig. 3, which is shown in detail in Fig. 5, was the same design in all the electroscopes. It consisted of a fixed blade *A* of brass, to the upper end of which was soldered a brass plate *B*. This plate served to give a sharp line of attachment for the aluminum leaf *L*, 10 mm. wide and 60 mm. long. The leaf was fastened to *B* by means of turpentine which had been exposed to the air.

The frame was securely mounted on a heavy wooden base, as shown in Fig. 8, by means of four bolts. This base also supported the cradle for the reading microscope, by means of which the position of the leaf was ascertained.

The reading microscope consisted of a Ross, 1.5-inch objective and 2-inch eyepiece, mounted in an ordinary draw-tube. The eyepiece contained a scale which was divided into 100 divisions.

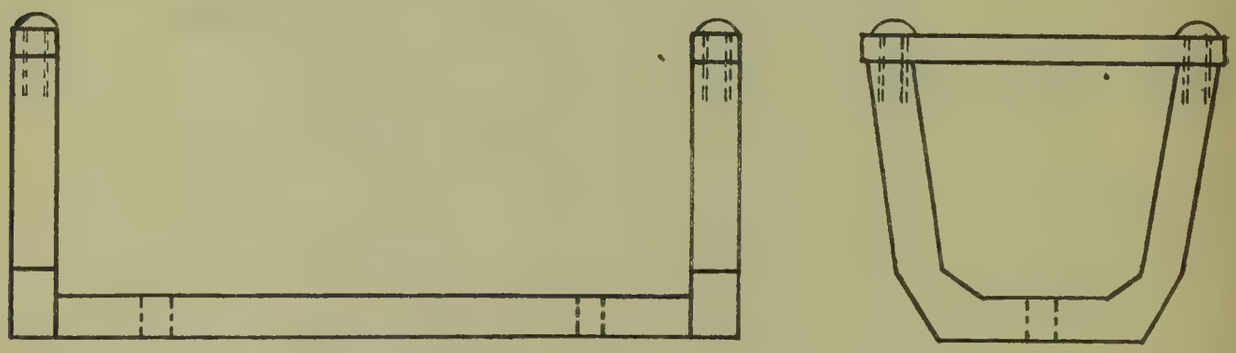


Fig. 6. Cradle for reading microscope.

The same reading microscope was used for electroscopes Nos. 2, 5 and 8. The cradle, Fig. 6, was fastened to the wooden base of the electroscope by means of two screws. By means of this device the reading microscope could be removed and remounted in the same position, with no change in the calibration of the instrument.

Electroscope No. 4: Electroscope No. 4 was of a design which has not, to my knowledge, been described in the literature. It was constructed by Prof. Herman Schlundt, and consisted of a rectangular brass frame with plate glass front and back (Fig. 7), similar to the Boltwood form. The frame was provided with two large brass stop-cocks, made by A. Pfeiffer, Wetzlar. The upper end of the leaf system was fastened into a hollow cylinder, threaded so as to fit a brass ring by means of sulphur which served as the insulator. A small brass cap for the protection

of the insulation was fitted over the projecting end of the brass rod of the leaf system. The electroscope was charged by touching the projecting rod of the leaf system, the case being earthed.[49] The volume calculated from the internal dimensions of the case was 955 c.c., by actual measurement 952 c.c.

The electroscope was provided with a reading microscope, a Bausch & Lomb combination of a 32-mm. objective and 2-inch eyepiece mounted in a draw-tube. The microscope was mounted in a collar soldered to a circular rod, which was held in position in a socket by means of a set-screw. This form of mounting did not possess the rigidity shown by the cradle mounting with

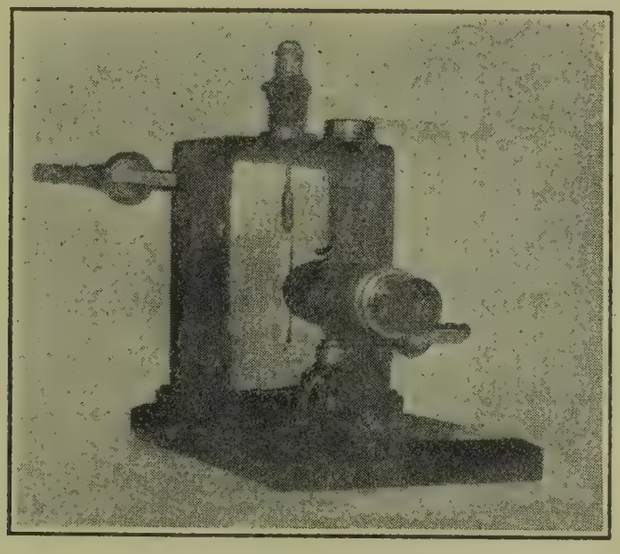


Fig. 7. Electroscope No. 4.

which the other instruments were provided. Moreover, in case the microscope was disturbed, the instrument had to be restandardized.

Electroscope No. 5: Electroscope No. 5 (Fig. 8) was constructed after the design of Schmidt.[50] It consisted of a cylindrical brass vessel fitted with two stop-cocks. The top of the vessel could be removed, and the bottom carried a threaded brass ring, through which the electrode of the leaf system projected and by means of which it could be attached to the frame of the electroscope by a rubber washer. The leaf system consisted of a brass plate, carrying the aluminum leaf mounted as

[49] The electrostatic capacity of this form of electroscope may be changed by screwing a rod or plate to the upper end of the projecting part of the leaf system.

[50] Schmidt, H. W., Physik. Z., **7**, 157 (1905).

before, attached to a brass rod. The rod of the leaf system passed through a sulphur plug in the top of the frame, and carried on its upper end a central electrode 1 cm. in diameter and 15 cm. in length. The frame was fastened to a wooden base which carried the cradle for the reading microscope.

This instrument showed the "crawl effect," described later, to a marked degree. The leaf was also disturbed by air currents and outside electrical disturbances, which made the measurements

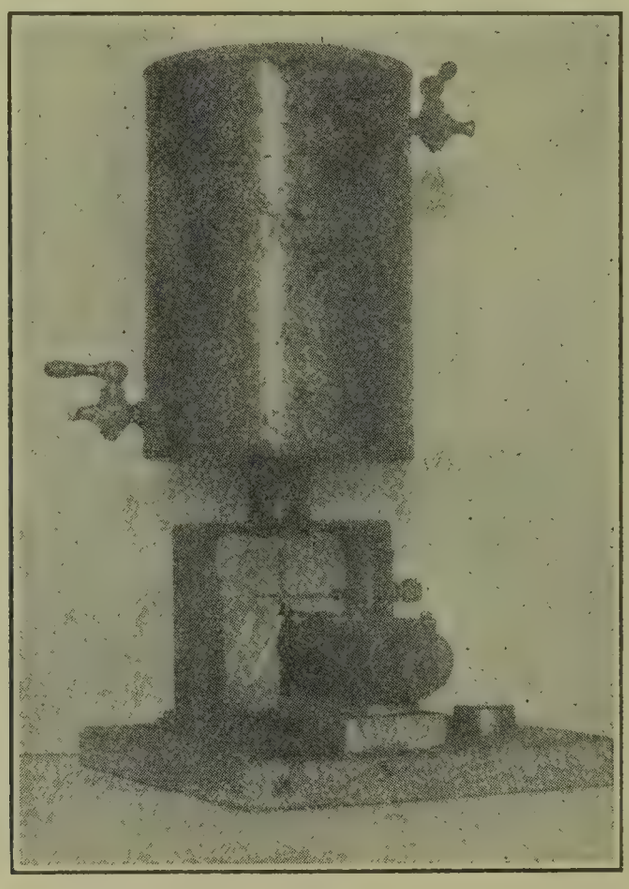


Fig. 8. Electroscope No. 5.

with this instrument more or less unsatisfactory. The data obtained were added for completeness and for their qualitative value only.

Electroscope No. 8: This instrument, of the same general design as No. 4, but with a smaller ionization chamber, was the most reliable electroscope used. The same frame as was used for electroscope No. 2 was used. The glass tube and leaf system were removed and replaced by a simplified leaf system similar to that of No. 4.

DETERMINATION OF THE ELECTROSTATIC CAPACITY OF THE ELECTROSCOPES.

The Standard Capacity: For determining the capacity of the electroscopes, a calibrated Harmes condenser was used. The Harmes condenser[51] consists of an inner cylinder supported upon an amber block, surrounded by an outer cylinder insulated by vulcanite. The inner cylinder is provided with an electrode which projects thru an opening in the outer cylinder. The whole is enclosed in a metal case, which is kept grounded in order to avoid outside electrical disturbances.

Sources of Potential: As a source of potential, storage cells and dry batteries were used. The set of storage batteries consisted of 99 cells, connected in series so as to furnish approximately 200 volts. Two 4-candle-power lamps were placed in the circuit to avoid accidental short-circuit of the storage cells.

As it was necessary to carry out these experiments with potentials over 200 volts, two boxes of dry cells were added. Fifty sets, 150 batteries,[52] were placed in a box and insulated by means of a glass plate in the bottom and glass rods between the sets. These dry batteries furnished an additional potential of about 400 volts, so that in all about 600 volts were available.

Determination of the Potential of the Battery and Calibration of the Scales of the Electroscopes: For determining the potential of the charging batteries, a voltmeter reading to 300 volts[53] was used, correct by standards to 0.2 volt up to 150 volts.

Two difficulties presented themselves: First, the potentials used were greater than could be registered on the voltmeter; and, scond, the current used by the voltmeter caused an appreciable drop of the potential.

In order to overcome the first difficulty the battery was divided into three sections, the storage batteries SB, and dry battery sets DB 1 and DB 2. The electromotive force of each section was determined separately.

Since the determination of the electromotive force of the

[51] Harmes, F., Physik. Z., **5**, 47 (1904). Instrument No. 2240 furnished by Gunther and Tegetmeyer of Braunschweig. Capacity, charged by induction, 42.5 centimeters.

[52] Columbia Flash Light Batteries No. 03, made by National Carbon Co., Cleveland, Ohio.

[53] Voltmeter No. 74504. American Instrument Co., Type 4, scales 0-3, and 0-300. Resistance of voltmeter 0-300 scale was about 30,000 ohms.

batteries also involved the calibration of the scales of the electroscopes, these two operations will be described as one.

The electroscopes were leveled by means of a small circular level placed on the case. The negative pole of the storage batteries SB was placed in contact with the leaf system of the electroscope. In the case of electroscopes Nos. 4 and 8 the contact was made with the projecting rod of the leaf system. In the case of electroscopes Nos. 2 and 5 the glass back of the frame was temporarily replaced by a glass plate having a small hole 7 mm. in diameter opposite the fixed blade of the leaf system. The positive pole of the storage batteries was connected to the negative of DB 1, and the positive of DB 1 to the negative of DB 2. The case of the electroscope was earthed, and to the earth connection was attached a traveling electrode, which could be attached to any of the several points where the dry batteries were soldered together.

The negative terminal of the voltmeter was attached to the negative terminal of DB 2, and the positive terminal to the traveling electrode. The traveling electrode was now attached to the several points of the battery in succession, and the position of the leaf with the voltmeter in and out of circuit was now noted for the several points. From the difference of the scale reading with the voltmeter in and out of circuit and the approximate value of one scale division the drop of potential due to the internal resistance of the batteries was calculated, and then added to the voltage observed when the voltmeter was in circuit for that point. This gave the electromotive force for zero current of that portion of DB 2 which was used.

The electromotive force of DB 1 and at the storage batteries was determined in the same way. The method of calculation will appear clear from the specimen set of data given in Table I.

TABLE I.

Data for Calibration of the Scale of Electroscope No. 2.

	V.		S_1			S_2	$S_2 - S_1$		V corr.	E_1	E_2
	1	2	3	4	5	6	7	8	9	10	11
a	170		84.0			93.0	9.0	9.3	179.3	365.8	375.1
b	154	16	68.5	15.5	1.03	77.0	8.5	8.8	162.8	349.8	358.6
c	142	28	57.5	24.5	1.05	64.5	7.0	7.2	149.2	337.8	345.0
d	126	44	41.5	42.5	1.03	48.0	5.5	5.7	131.7	321.8	327.5
e	114	56	29.0	55.0	1.02	35.0	6.0	6.2	120.2	309.8	316.0
f	101	69	18.5	66.5	1.04	23.0	4.5	4.6	105.6	296.8	301.4
g	87	83	4.0	80.0	1.04	7.0	3.0	3.1	90.1	282.8	285.9
f	103	69	19.0	67.0	1.03	23.0	4.0	4.1	107.1	298.8	302.9
d	124	56	40.0	56.0	1.00	45.0	5.0	5.2	129.2	319.8	325.0
c	144	28	59.5	26.5	1.05	65.0	5.5	5.7	149.7	339.8	345.5
b	164	16	78.0	16.0	1.00	83.0	5.0	5.2	169.2	359.8	365.0
a	172		86.0			92.5	6.5	6.7	178.7	367.8	374.5
SB	185		82.0			92.5	10.5	10.8	195.8		

DB 2 was not used. The points a, b, etc., were taken from DB 1.

Column *1* of the table gives the voltage as read off the voltmeter. Column *2* gives the increment in V, column *1*. Column *3* gives the scale reading S_1 corresponding to V. Column *4* gives the increment of S_1 referred to initial value of S_1. Column *5* gives the approximate value of one scale division as calculated from columns *2* and *4*. Column *6* gives the scale reading with the voltmeter out of circuit corresponding to S_1. Column *7* gives the difference S_2—S_1. Column *8* gives the difference reduced to volts by multiplying by the mean of column *5*. Column *9* gives the electromotive force of the section of the battery measured by the voltmeter. Column *10* gives the total electromotive force corresponding to S_1. Column *11* gives the electromotive force corresponding to S_2. When E_1 was plotted against S_1, and E_2 against S_2, all the points fell in a straight line.

Later in the investigation, one of the electroscopes was used as an electrostatic voltmeter for determining the electromotive force of the battery. The dry batteries were found to give satisfactory results for this work if care was used not to leave the voltmeter in circuit for more than two minutes.

Schmidt[54] has pointed out that the potential registered by an

[54] Schmidt, H. W., Physik. Z., **7**, 157 (1905).

electroscope may not be proportional to the scale divisions. This conclusion has been verified in the case of electroscope No. 4. With three different aluminum leaves it gave calibration curves which were not straight lines. The calibration curves obtained with electroscopes Nos. 2, 5 and 8 were straight lines, and the potential between the limits of calibration was proportional to the scale reading. The specific factors which effect the form of the calibration curve obtained for different electroscopes have not been ascertained; however, it appears that the form of curve obtained will depend upon the form, size and shape of the individual electroscope as well as upon the properties of the leaf itself.

The Electrostatic Capacity of the Electroscope: For finding the electrostatic capacity of the electroscopes the method of Harmes[55] was used. The joint capacity of the leaf system and the condenser was first determined.

The case of the electroscope was earthed and the negative pole of the battery, arranged as before, placed in contact with the leaf system as described for calibrating the scale. The movable electrode was attached to the battery so that the leaf would be near the upper end of the scale. The position of the leaf (S_1) was read on the scale and the voltage of the battery (V_1) determined by reference to the curve sheet for the particular electroscope. The outer protecting case of the condenser and the leaf system of the electroscope were then earthed. The outer cylinder of the condenser was then charged by means of the battery whose electromotive force had just been determined as above. The inner cylinder of the condenser was earthed. After at least two minutes, the earth connection with the leaf system of the electroscope and with the inner cylinder of the condenser were broken. The connection between the battery and the outer cylinder of the condenser was then broken, and the outer cylinder earthed.

The electrode of the inner cylinder was now touched to the leaf system of the electroscope, and the position of the leaf (S_2) noted. The potential (V_2) was determined by reference to the curve.

[55] Harmes, F., *Loc. cit.*

The joint capacity

$$K = \frac{CV_1}{V_2} \tag{2}$$

in which (C) is the capacity of the condenser of 42.5 centimeters, and (K)[55(a)] the joint capacity.

For the determination of the electrostatic capacity of the electroscope, the inner cylinder of the condenser was placed in contact with the leaf system of the electroscope; the outer cylinder and case of the condenser, and the case of the electroscope were earthed. The condenser was now charged so that the leaf came on the upper part of the scale of the reading microscope. The position of the leaf was noted. The contact with the leaf system was broken and the condenser removed several feet from the electroscope. The position of the leaf (S_{12}) was noted and the leaf earthed for at least two minutes. The electrode of the inner cylinder was again brought in contact with the leaf system and the reading (S_{13}) noted. The potentials (V_{11}), (V_{12}), and (V_{13}) corresponding to the scale readings (S_{11}), (S_{12}) and (S_{13}) were obtained by reference to the curve for the particular instrument used. The capacity

$$C_1 = \frac{K(V_{11} - V_{13})}{V_{12}} \tag{3}$$

The condenser was charged by induction to a potential of 593 volts. This charge, divided between the leaf system of electroscope number four, gave a reading on the scale of 0.0 or 416 volts. From this data the joint capacity (K) is 60.6 centimeters.

The condenser and leaf system were charged to a potential (S_{11}) on the scale of 95.0. On removing the condenser (S_{12}) was 91.0. The leaf was earthed for two minutes, insulated, and the charge on the condenser divided. The reading (S_{13}) was 33.2. The voltages (V_{11}), (V_{12}), and (V_{13}) were 588.4, 583, and 485.3 respectively, or the capacity of electroscope number four without cap[55(b)] was 10.7 centimeters.

[55](a). K is not the sum of the capacities of the condenser and electroscope, as was pointed out by Harmes.

[55](b) Some of the determinations in number four electroscopes were made with the cap in place. The readings (S_{21}) were made with the electroscope charged without cap. The cap was now fitted in place and the reading (S_{22}) taken. A determination gave (S_{11}) as 97.0 and (S_{22}) as 82.7. (V_{21}) and (V_{22}) were 593 and 571 volts. The capacity of the electroscope with cap C_1 is given by the equation

$$C_1V_{22} = CV_{21}.$$

from which (C_1) is 11.1 centimeters.

The results of the determination of the electrostatic capacity are shown in the table. The mean of several determinations are given in each case.

TABLE II.

Capacity of the Electroscopes.

No. of Electroscope	Joint Capacity K. Cm.	Capacity C. Cm.	Capacity with Cap. C_1 Cms.
2	48.9	3.01	
4	60.6	10.7	11.1
5	74.6	14.8	
8	53.4	6.13	

A "Crawl" Effect. During the early part of the investigation it was observed that the leaf, after being charged, and the battery left in contact, slowly increases its apparent potential. It was at first thought that this effect might be due to a change in the potential of the dry batteries used. The voltmeter was then connected across the terminals of the dry batteries and although the voltage remained constant the effect was still observed on charging the leaf. Later it was found that if the leaf was discharged and then the condenser with the inner cylinder charged was brought in contact with the leaf, that the same effect was still observed. The amount of increase was in some cases as much as twenty-five volts. The effect was most marked in electroscope No. 5, but was also observed in Nos. 2, 8 and 4. The potential finally rose, after from two minutes to three hours, to a definite maximum for each point of the charging battery. If the electroscope was kept charged for a long time and then only partly discharged and again charged, the maximum value of the potential was reached very much quicker.

This "crawl effect" made the determination of the capacity of the electroscopes very troublesome and uncertain in those electroscopes in which it was observed to the greatest extent, Nos. 2 and 5. The electrostatic capacity of Nos. 4 and 8 were very much easier to determine, both on account of the lesser "crawl effect" and on account of the fact that the leaves could not be disturbed by air currents.

It was thought that the effect observed might be due to induced

charges on the surface of the glass plates forming the front and back of the electroscopes. A copper gauze was fitted inside the plates and grounded, but the effect was still observed. No further experiments to determine the cause of the effect were carried out, but it may be due to some inherent property of the sulphur insulation used.[56]

The only reference which could be found in the literature which suggested the existence of such an effect was one by Dike.[57] He mentioned that in calibrating his apparatus for measuring atmospheric electricity (Gerdian electroscope insulated by means of amber) he waited one minute during the charge of the leaf for all the charges on the insulation to become neutralized, but he made no specific mention of an upward "crawl" of the leaf after charging. I had observed before the above paper had appeared, that in order to obtain concordant results in the determination of the electrostatic capacity of the electroscopes, it was necessary to leave the leaf system insulated for at least two minutes, when it was discharged.

This anomalous behavior of these electroscopes may have some bearing on observation recorded by Schlundt and Moore in one of their papers.[58] They state that at the maximum activity of a sample of radium emanation, three hours after its introduction into the electroscope, that the activity of the samples apparently increased during the first five minutes after the leaf was first charged, and that if the electroscope was allowed to stand discharged one hour and the observations repeated the same readings would be obtained. This result was tentatively explained by Schlundt and Moore as probably due to the concentration of an additional quantity of one of the products of rapid decay of the emanation upon the charged leaf system, thus causing slightly more ionization in the immediate vicinity of the leaf. This increase in activity was also observed in my experiments, but it may be explained in a somewhat different manner. The above mentioned anomalous upward "crawl" of the leaf during the first few minutes after charging, would tend to

[56] Later in the summer of 1909, Prof. Schlundt in working with the Ebert form of ionization apparatus obtained similar effects. The insulation in this type of apparatus is of amber. When the moisture was removed from the electroscope by means of metallic sodium, the effect was not observed.

[57] Dike, P. H., Science, **29**, 475 (1909); Am. Jour. Sci., March, 1909.

[58] Schlundt and Moore, Trans. Am. Electrochemical Soc., **8**, 292 (1905).

counteract the fall of the leaf due to the ionization current. Since it was observed that the leaf reached its maximum in a shorter time, if the electroscope had been charged for a time, the effect of the "crawl" would become less noticeable after two or three readings had been taken, and the time to pass a given number of divisions would become shorter.

Stewart has pointed out[59] that when quadrant electrometers are used for measuring current, that the needle must be allowed to swing at least twenty-five seconds before readings of the velocity of the needle can be taken. This precaution was taken so that the needle could reach a uniform velocity. In like manner it would appear from these experiments that on account of the "crawl" effects, the leaf of the electroscope must be charged

TABLE III.

Time Secs. x 10 ^{3}	Time to fall 1 Div. Secs.	Time Secs. x 10^{-3}	Time to fall 1 Div. Secs.
0	charged	20.12	recharged
0.05	16	20.31	88
0.61	39	21.04	146
1.59	61	21.78	180
1.80	65	22.02	recharged
3.58	73	22.12	80
4.58	91	22.36	105
8.50	recharged	22.52	138
8.53	36	22.75	discharged
8.96	50	26.68	recharged
10.33	72	26.71	16
11.06	84	26.81	36
13.03	101	26.86	44
14.00	recharged		
14.30	52	27.25	recharged
14.55	65	27.34	70
15.22	94	27.54	78
18.09	123	27.71	86
19.43	212	27.95	86

to a sufficiently high potential to give from one-half to three minutes before the leaf comes upon the scale of the microscope. When this precaution was taken very concordant readings were obtained.

Anomalous Air-Leak. Another anomaly in the behavior of the electroscopes was observed to a slight extent with all the instruments, but more especially with Nos. 5 and 8. It was noticed that the air-leak in these electroscopes, which was rather

[59] Stewart, O. M., Physic. Rev. **21**, 229 (1905).

high, apparently decreased after the leaf had been charged for some time. Several series of determinations were then taken of the air-leak over periods of about seven hours. The results of several such series were always similar in their general tendency, but no relation could be deduced as regards the magnitude of the change in the natural air-leak.

One of the series of observations which shows the effect in the largest degree is reproduced in Table III.

The electroscope which was used had not been charged for three days previous to the measurements given. Column *1* gives the time in seconds after the leaf was given its first charge. Column *2* gives the time required in seconds to fall one scale division.

It will be observed that the air-leak grows less as the time the electroscope has been charged increases, and that if the electroscope is left discharged for a short time, the same phenomenon is observed but in a less degree. It was thought that these results might be due to dust, but sweeping the electroscope out with dust-free air did not have any effect.

The effect of this disturbance was just opposite to that of the anomaly described above. In this case the uncertainty of the air-leak was overcome during the regular experiments by keeping the leaf charged by means of the battery during the interval between the introduction of the emanation and the final measurement. The concordant readings of time to fall the usual number of divisions, which were usually obtained after some five or ten minutes, were taken as the measure of the activity. On account of the lack of time, this air-leak effect was not further investigated.

EXPERIMENTAL DETERMINATION OF THE RELATION BETWEEN THE BOLTWOOD EMANATION STANDARD AND THE C. G. S. ELECTROSTATIC STANDARD.

After the introduction into the electroscopes of the radium emanation, which had been boiled off from the standard samples of uraninite in the various forms of apparatus, as described in the previous sections, the ionization was allowed to reach a maximum value, which required three hours. After this time, the time for the leaf to fall a given number of divisions in the

eye-piece, usually from 100 to 50 in the case of electroscope No. 4, and from 100 to 20 in the other instruments was noted with a stop-watch. As soon as the measurements upon the emanation were completed the stop-cocks were opened and a slow current of dry air led thru the elctroscopes. From the calibration curve the scale readings were reduced to potential readings, from which the number of volts fall per second was calculated. From this result was subtracted the number of volts fall of potential per second due to the normal air leak, determined in each case just before the introduction of the emanation into the electroscope.

The current was then computed from the following equations:

$$i = \frac{C\,d}{300}\ C.\ G.\ S.\ E.\ S.\ U. \qquad (4)$$

or

$$i = \frac{C\,d}{9 \times 10^{11}}\ \text{amperes.}^{60} \qquad (5)$$

where C is the capacity of the electroscope in electrostatic units, and d the number of volts fall of potential per second, due to the ionization produced by the radium emanation and its products in equilibrium.

The current produced by the radium emanation in equilibrium with one gram of uranium, or 3.4×10^{-7} gram of radium, was found by the equation:

$$I = \frac{i}{\text{wt. of } U.} \qquad (6)$$

where I is the measured ionization current for the radium emanation and products in equilibrium with one gram of uranium in a mineral.

The results thus calculated are given in Table IV columns *5* and *6*. Column *1* gives the number of the sample, column *2* the apparatus in which the emanation was boiled off, column *3* the number of the electroscope used, and column *4* the grams of uranium in the sample. The results of all the determinations are given.[61]

[60] Rutherford, E., Radioactivity, p. 100.

[61] In some cases the apparatus was known to have been tampered with and these results are not given at all.

TABLE IV.

Results of Electroscopic Determinations.

1 No of Sample	2 App. for Sep. Emanation	3 No. of Electroscope	4 Grams *U.*	5 *I* Amps. x 10^{10}	6 *I* C. G. S. E. S. U.
1 A	S. & M.	4	0.01	4.10	1.23
2 A	S. & M.	4	0.01	4.34	1.30
3 A	S. & M.	2	0.01	2.36	0.71
5 B	Strutt	4	0.01	3.08	0.92
6 A	Strutt	5	0.025	4.45	1.34
7 A	Strutt	5	0.025	4.37	1.31
8 A	S. & M.	4	0.025	4.41	1.32
10 A	Strutt	4	0.035	2.98*	0.89*
11 A	Strutt	2	0.035	2.11	0.63
12 A	S. & M.	4	0.035	4.72	1.42
13 A	S. & M.	4	0.05	4.80	1.44
15 A	Strutt	4	0.05	3.93	1.18
18 A	S. & M.	8	0.1	3.01	0.90
19 A	S. & M.	8	0.15	3.08	0.92
23 C	S. & M.	2	0.01	1.71*	0.51*
25 C	Strutt	4	0.01	3.04	0.91
27 C	S. & M.	4	0.01	1.97*	0.59*
28 C	Strutt	8	0.01	2.09	0.63
30 C	Strutt	8	0.025	2.08	0.62
31 C	Strutt	8	0.025	2.55	0.77
33 C	Strutt	8	0.025	2.33	0.70
34 C	S. & M.	5	0.025	3.90	1.17
35 C	S. & M.	5	0.025	3.81	1.14
36 C	S. & M.	8	0.025	2.68	0.80
37 C	S. & M.	8	0.05	2.92	0.88
38 C	Strutt	4	0.05	3.17	0.95
39 C	S. & M. Water	8	0.05	1.57	0.47
40 C	Strutt	5	0.05	2.04*	0.61*
41 C	S. & M.	5	0.10	4.26	1.28
42 C	Strutt	8	0.10	2.51	0.75
43 C	S. & M.	5	0.10	3.06	0.92
44 C	S. & M.	4	0.01	3.18*	0.94*
45 C	Strutt	8	0.025	2.28	0.68
46aC	S. & M. Water	5	0.025	3.40	1.02
46bC	S. & M.	4	0.025	2.49*	0.75*
56 D	Boltwood	4	0.0563	4.10	1.23
58 D	Boltwood	4	0.0632	3.68*	1.10*
75 E	S. & M. Water	8	0.0565	2.48	0.72
77 E	S. & M.	5	0.112	4.82	1.45
74 E	McCoy	8	0.0632	2.54	0.76
Determinations on Emanation Occluded by Uraninite.					
1S″[62]	S. & M.	4	0.0265	4.23	1.27
2S″	S. & M.	4	0.0265	3.85	1.16
3S″	S. & M.	4	0.0265	4.44	1.33
4S″	S. & M.	4	0.0265	4.59	1.38

[62] I am indebted to Prof. Herman Schlundt for these determinations, Nos. 1S″ to 4S″.

It will be noted that some of the experiments are starred (*), and these for various reasons are not considered as reliable as the others.

The mean results of the determinations for each type of apparatus, each electroscope, and each weight of uranium taken as a sample are given in Table V.

TABLE V.

No. of Samples	No. Electroscope	Grams U	Mean I Amps. x 10^{10}
Strutt Apparatus.			
11 A	2	0.035	2.11
5 B, 25 C	4	0.01	3.06
15 A, 38 C	4	0.05	3.55
6 A, 7 A	5	0.025	4.41
28 C	8	0.01	2.09
30 C, 31 C, 33 C, 45 C.	8	0.025	2.31
42 C	8	0.1	2.51
Schlundt and Moore Apparatus.			
3 A	2	0.01	2.36
1 A, 2A	4	0.01	4.22
8 A	4	0.025	4.41
12 A	4	0.035	4.72
13 A	4	0.05	4.80
34 C	5	0.025	3.86
41 C	5	0.10	4.26
77 E	5	0.112[63]	4.82
36 C	8	0.025	2.68
37 C	8	0.05	2.92
18 A	8	0.1	3.01
19 A	8	0.15	3.01
Schlundt and Moore Apparatus for Water Samples.			
46 aC	5	0.025	3.40
39 C	8	0.05	1.57
75 E	8	0.0565[63]	2.48
Boltwood Apparatus.			
56 D	4	0.0563[63]	4.10
58 D	4	0.0632[63]	3.68
McCoy Apparatus.			
74 E	8	0.0632[63]	2.54
Schlundt and Moore "Standardizing."			
1 S", 2 S", 3 S", 4 S"	4	0.265	4.28

[63] These samples were not stored until the maximum amount of emanation had accumulated. The weight of uranium given in weight which would give at equilibrium the same amount of emanation as has accumulated in the sample.

In general the results obtained with electroscope No. 8 are the most reliable. This electroscope was practically free from the anamolous effects described above. The rate of fall of the leaf with this type of electroscope is very regular. The leaves act rapidly, getting into position in ½ to 1 minute; sometimes nearly right in 1 to 2 seconds.

The current I in amperes per gram uranium for this electroscope is shown plotted against the grams uranium in the sample in Fig. 9. Electroscope No. 4 of the same general form as No. 8 gave results which were nearly as satisfactory. It was found

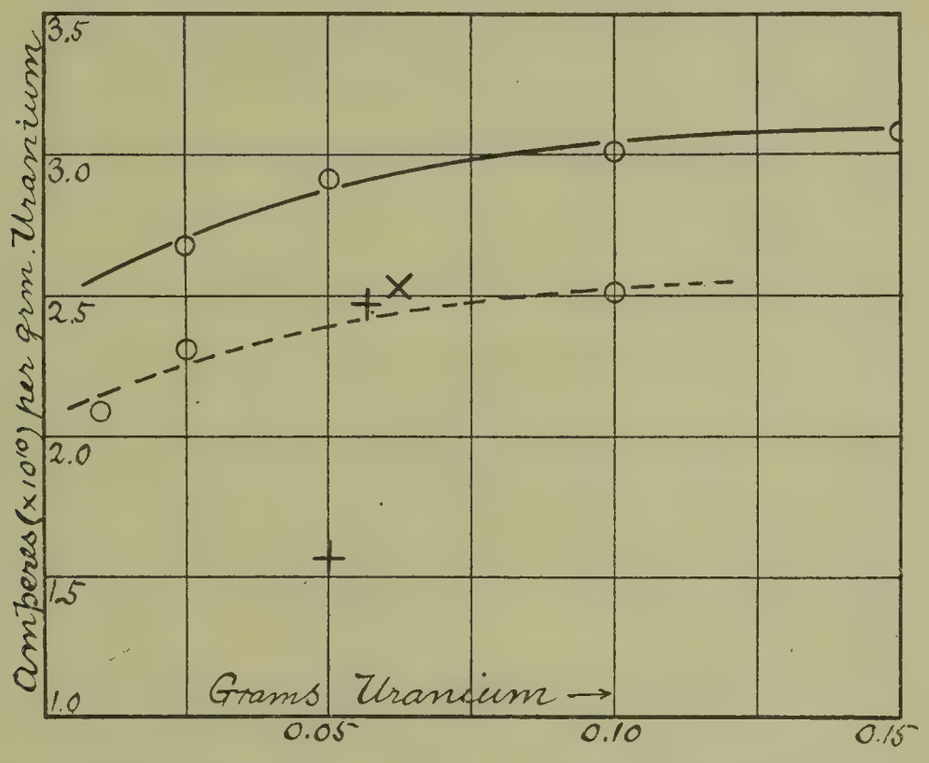


Fig. 9. Ionization Current per gram Uranium, Electroscope No. 8.
——— Schlundt and Moore Apparatus.
— — — Strutt Apparatus.
\+ Schlundt and Moore Apparatus for Water Samples.
× McCoy Apparatus.

that the form of mounting for the reading microscope was not so satisfactory as the cradle mounting used on the other instruments. The results obtained with this instrument are plotted in Fig. 10. Only two determinations were obtained with electroscope No. 2 before it was converted into electroscope No. 8. The soft iron wire by means of which the electroscope is charged did not always take the same position relative to the leaf,[64]

[64] Any object on the inside of the electroscope which is not rigidly fastened to the case is objectionable. The electroscope described by Joly (Radioactivity and Geology) is open to this objection.

although the case was leveled before each reading. The effect of a change in the position of the iron wire is to change the electrostatic capacity and hence the constant of the instrument. The results obtained with electroscope No. 5 are entitled to qualitative consideration only.

The Schlundt and Moore apparatus for separating the emanation gave uniformly higher ionization currents than any of the other forms of apparatus. The ionization current using the Strutt form was approximately 25 per cent. lower than when the Schlundt and Moore form was used.

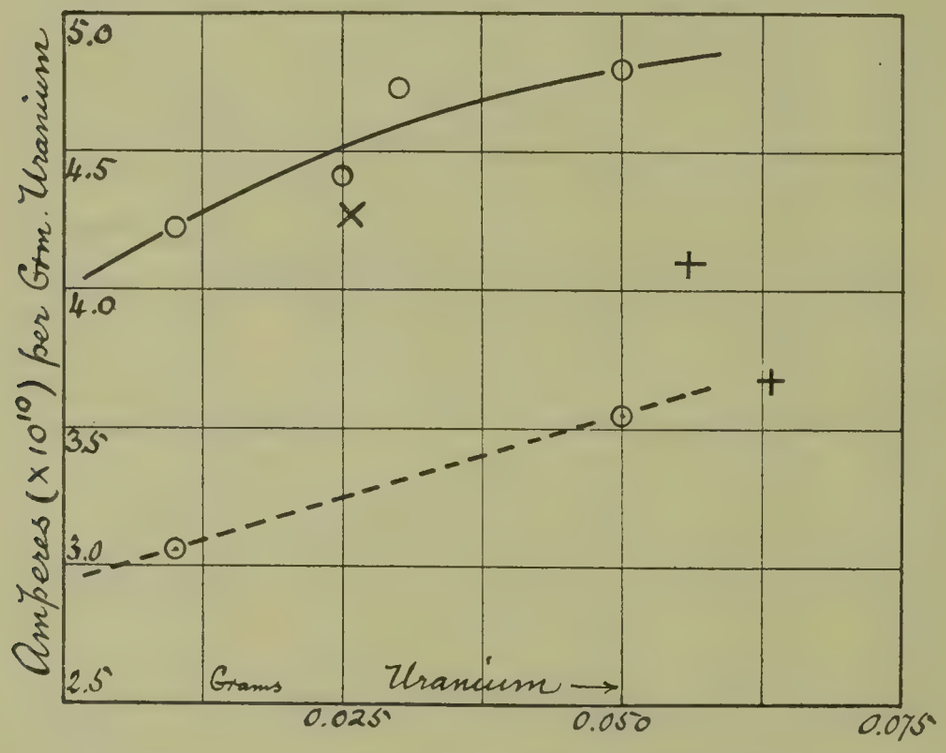


Fig. 10. Ionization Current per gram Uranium, Electroscope No. 4.

——— Schlundt and Moore Apparatus.
— — — Strutt Apparatus.
\+ Boltwood Apparatus.
× Schlundt and Moore "Standardizing" Apparatus.

Two samples boiled off in the Schlundt and Moore apparatus for water samples were measured in electroscope No. 8. The first sample number 39C was boiled, but the steam was not allowed to completely displace the water in the bulb.[65] The water in the collecting bulb and side tube thus did not reach the boiling point. It will be noted that a very low current was obtained in this case. Sample number 75E was boiled from the bulb. The current in this case is much higher, and lies almost

[65] Schlundt and Moore, *Loc. cit.*

on the curve for the Strutt apparatus. One sample, number 74E, was boiled off in the McCoy apparatus, and measured in this electroscope. The current in this case was lower than that obtained by the use of the Schlundt and Moore apparatus, but higher than that obtained with the Strutt apparatus. Two determinations using the Boltwood apparatus were made. The results are similar to those obtained with the Strutt apparatus.

The determinations *13* to *43* were carried out by collecting the emanation occluded in samples of the uraninite in the Schlundt and Moore form of burette.[66] The value of the ionization current per gram of uranium is somewhat less than the equilibrium amount obtained by storing the solution forty days. The smaller value may be due to the constant loss of emanation by the powdered mineral at ordinary temperatures. It will also be noted that the results are not as concordant as those obtained by storing the solution of the mineral and then separating the emanation.

The curves Figs. 8 and 9 on the whole show that the ionization observed in the electroscope is not proportional to the quantity of emanation originally in equilibrium with the sample. Since if the potential used was not sufficient to give the saturation ionization current there would be more recombination of the ions at higher concentrations of the radium emanation than at low concentrations, the ionization current at higher concentrations would then be relatively lower, which is contradictory to the observed facts. The discrepancy may be explained, however, by assuming that there was relatively more absorption of the radium radiation by the water through which the gas bubbled in the separating apparatus, in the case of the samples of smaller concentration. The fact that at the same concentration different quantities of the emanation are separated by the various forms of separating apparatus also seems to indicate that absorption of the emanation may be the cause of the discrepancy.

Joly[67] has devised an apparatus in which the emanation is boiled off under reduced pressure. Joly has found that successive standardizing experiments gave sensibly the same constant for his electroscope even when the quantities of emanation introduced

[66] Schlundt and Moore, *Loc cit.*

[67] Joly, J. Radioactivity and Geology, p. 260. This work appeared after the experimental work described in this paper was completed.

were varied largely. Fletcher,[68] using the Joly apparatus, found that standardizing experiments with 1 mg. and 4 mg. uraninite gave the same constant for his electroscope. Uraninite was then dissolved and added to solutions similar to those used in determining the radium content of minerals. When the emanation was separated from these solutions, higher constants for the electroscope were then obtained.

The quantity of emanation separated in the forms of apparatus described is reproducible at any concentration of emanation, and one may safely use any one apparatus so long as the experimental conditions such as composition of the solution, concentration of radium emanation, time of boiling, etc., are reproduced in the standardizing experiments. The Schlundt and Moore apparatus gave the more uniform results in my hands.

The values for the average ionization currents per gram of uranium when the emanation in equilibrium with 0.05 grams uranium was separated in the Schlundt and Moore apparatus are given in column *2* of Table VI. The electrostatic capacity

TABLE VI.

No. of Electroscope	*I* per Gram Amps. x 10^{10}	Electrostatic Capacity, Cm.	Volume in C. C.	I/V
2	2.36	3.01	590	0.0039
4	4.80	10.7	952	0.0050
5	4.80	14.8	2840	0.0017
8	2.92	6.13	565	0.0052

of the electroscopes is given in column *3*. The volume of the ionization chamber was determined directly, and is given in column *4*. The ratio of the ionization current to the volume is given in column *5*. No relation is apparent betweeen the electrostatic capacity and the ionization current. For the small electroscopes Nos. 4 and 8, which were of like design, the ionization is nearly proportional to the volume. However, if we consider electroscopes Nos. 2, 5 and 8, which were all of different designs, no proportionality between the ionization current and the volume exists. The proportionality between the volume and the ionization current in the case of electroscopes 4 and 8 is probably only accidental.

We have seen above that if all the radiation from the emana-

[68] Fletcher, Arnold L., Phil. Mag., **20**, 36 (1910).

tion and half that from the active deposit were absorbed in air we should expect a value of 6.18×10^{-10} amperes or 1.854 C. G. S. electrostatic units for the ionization current per gram uranium, which corresponds to $6.18 \times 10^{-10}/3.4 \times 10^{-7}$ or 1.82×10^{-3} amperes per gram of radium. The approximate limiting values, as determined from the curves for the Schlundt and Moore apparatus alluded to, for the ionization current per gram uranium when large quantities are separated, are given in column *2* of Table VII. The ration of the observed ionization current for any electroscope to that calculated above, *i. e.*, 6.18×10^{-10} amperes, will give the fraction of the maximum radiation absorbed in air. This ratio we may call the "ionization efficiency" of the electroscope. The percentage efficiency so calculated is given in the last column of the table. As was to be expected,

TABLE VII.

Ionization Efficiency of the Electroscopes.

No. Electroscope	Limiting I Amps. $\times 10^{10}$, per G. U.	Efficiency, Percent
2	2.4	39
4	4.9	79
5	4.8	78
8	2.9	47

those electroscopes with the larger ionization chambers, Nos. 4 and 8, were the more efficient. Nearly all determinations of the radioactivity of rocks, minerals, waters, sediments and other common materials have been made with electroscopes of the above and similar designs.

Joly[69] has attempted to translate the results of W. Knoche, who measured the activity of sea water, using a modified form of the Engler and Sieveking apparatus, and expressed his results in C. G. S. electrostatic units in terms of grams radium per liter. In this and other attempts of a similar nature it has been assumed that all the ionization was absorbed in the air of the ionization chamber. The above results show this assumption may lead to a very large error, and since it is the radioactivity and not the ionization current in a particular electroscope that is usually desired, those determinations expressed in C. G. S. electrostatic units lose their quantitative value.

[69] Joly, J., Phil. Mag. **18**, 396 (1909).

The ratio of the radium to uranium in an old mineral is constant, 3.4×10^{-7} grams of radium per gram uranium, and results expressed in terms of the Boltwood standard can be directly converted into terms of percent radium in the sample. It would thus appear that the Boltwood standard is the only standard easily available and capable of giving quantitative results for a standard of radioactivity of air, rocks, minerals, waters and other common minerals.

SUMMARY.

1. It has beeen experimentally shown that in general no constant relation exists between the Boltwood emanation standard and the C. G. S. electrostatic standard as ordinarily used.
2. The maximum ionization current produced in the ordinary electroscopes by the radium emanation and its products from an old mineral containing one gram uranium was calculated as 6.18×10^{-10} amperes, or 1.854 C. G. S. units.
3. For small electroscopes of the same design, the observed ionization current is nearly proportional to the volume of the ionization chamber.
4. The "ionization efficiency," *i. e.*, the ratio of the observed to the maximum ionization current, was found to vary between 39 and 79 percent for the electroscopes studied.
5. Several forms of apparatus for separating the radium emanation from its solutions have been studied, and the approximate efficiency of each form determined.
6. All the forms of apparatus for separating the emanation have been successfully improved, so as to avoid all loss of emanation in the transfer of the gas from the collecting bulb to the electroscope.
7. In standardizing the electroscopes it is necessary to so arrange the standardizing experiments that nearly the same quantity of radium emanation is boiled off as in the later determinations.
8. A new form of electroscope has been described and its merits proven.

9. An improved method of mounting the plate glass inserts in the brass frames of several types of electroscopes has been described.

10. A new form of cradle mounting for the reading microscope of electroscopes has been described.

11. It has been shown that in the case of some of the electroscopes the potential is proportional to the scale divisions over the range of the reading microscope. In other electroscopes this proportionality did not hold.

12. Small "flash-light" dry batteries have been used and found satisfactory as a source of potential for calibrating and charging electroscopes.

13. A peculiar "crawl" effect has been observed with electroscopes having sulphur insulation. The effect of this effect upon the rate of fall of the leaf has been pointed out.

14. An anomaly in the air-leak has been observed in some of the electroscopes used. The rate of leak decreased with the time-interval of charge of the leaf.

In conclusion the author wishes to express his gratitude to Prof. Herman Schlundt, of the Department of Chemistry, University of Missouri, for his kindly interest and helpful suggestions in accomplishing this study.

Chemical Laboratory, University of Missouri,
Columbia, Mo., January, 1912.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

UNIFORMITY AND SIMPLICITY IN ELECTROCHEMICAL AND ELECTROTHERMAL CALCULATIONS.

By Carl Hering.

One of the functions of a national society like the American Electrochemical Society is, or should be, to determine upon, or at least to recommend, standardization of terms, units, definitions, nomenclature, etc. The chief purpose of such standardization is to promote a clearer and more precise understanding of what the terms mean, to avoid ambiguity, to bring about uniformity, to reduce the number of alternative units for the same quantity, to simplify calculations, etc.; in general, the objects are precision and the conservation of mental energy.

Some problems, more particularly those pertaining to electrochemical and electrothermal apparatus, involve energy in various different forms, electrical, thermal, chemical, physical (change of state), mechanical, magnetic, luminous, etc.; they also involve power or rate of energy in various different forms, and transmitted in different ways, like in conduction, radiation, convection, induction, etc. In many cases these different forms of energy and power keep changing from one form to another. In general, each form has in the past been expressed or measured in terms and units peculiar to that form. When energy or power changes its form, however, it is still the same in amount, and it is an entirely unnecessary waste of mental energy to keep changing units as the energy changes form, which often involves repeated arithmetical conversion back and forth.

The purpose of the present paper is to urge simplicity and uniformity in such terms, units, expressions, etc., as are involved in calculations of this kind, and to urge that this Society, after duly considering the matter, make recommendations. Such action, it is believed, would aid greatly in the more general introduction and adoption of simplified methods.

In general, the simplification recommended by the writer is to use as our practical units some decimal multiple of the corresponding absolute unit. This was done by our forefathers, who established the excellent and simple system of electrical units in common use, all of which are decimal multiples of the absolute units; and every electrical engineer has cause to be thankful many times every day for the fact that his units were so chosen that no conversion factors (other than an occasional shifting of a decimal point and the unavoidable reduction from seconds to hours, and the reverse) are necessary, as they are all unity.

In the absolute system of units the chief features are the absence of practically all conversion factors, they being all unity, and the fact that there is one unit, and *only one,* for each physical quantity, which unit is a self-defined and a natural one. For energy, for instance, there is but one unit, the erg, no matter whether the form which the energy has is electrical, chemical, physical, mechanical, magnetic, luminous, etc. Similarly, power is always measured in ergs per second.

Hence if for our practical units we would adopt decimal multiples of these absolute units and discard all others, then all conversion factors would similarly drop out of our daily calculations. Such a complete change, altho desirable, would probably be too revolutionary to be acceptable, and would be likely to be dismissed as visionary idealism, altho probably no one would deny that it would be a desirable one to make if it were not for the inconvenience in making the change. Moreover, in such a radical change it is likely that even a new absolute system would be still better.

It is, however, well within our power to introduce at least a few easily made changes, and these alone will save us many daily calculations. The object of this paper is to point out and recommend some of these.

The first is to represent all power, no matter in what form it is, in terms of watts or kilowatts. Power is the rate of energy; it is energy divided by time. All forms of the generation, transmission or consumption of power would then be expressed in the same unit, whether they be electrical, thermal, chemical, mechanical, magnetic, luminous, etc., or whether the

transmission be by radiation, conduction, convection or otherwise. No troublesome conversion factors are then required. This change is already being made in some cases, and it is merely recommended here to extend its use much farther. The generation, consumption, flow, rate of loss, etc., of heat in electric furnaces or other electrothermal devices will then be expressed in watts or kilowatts instead of calories per second, B. T. U. per minute, etc., also the rate of consumption or production of chemical energy in an electrolytic cell. This change is particularly useful in connection with electric furnaces and other large electrochemical and electrophysical apparatus.

The second recommendation is to represent and measure all forms of energy in terms of the watt-hour or kw.-hour instead of in the two calories, B. T. U., etc. This would mean that all specific heats, latent heats, chemical energy popularly known by the inappropriate name "heats" of combination, etc., would be given in watt-hours or kw.-hrs. instead of in thermal units, thereby again avoiding all conversion factors.

Adopting the watt-hour or kw.-hr. for the practical unit of all forms of energy is not quite consistent with the absolute system, as this unit is not a decimal multiple of the absolute unit of time, the second; the adoption of the joule would be more rational. But in practice we have to deal with hours rather than seconds, and to adopt the joule would mean repeated multiplications and divisions by 3600 to change back and forth to watt-hours or kw.-hrs. As electrical energy in commerce and the industries is always expressed and measured in kw.-hrs. and not in joules, it is much less of a change, and will actually save many calculations to use the watt-hour and kw.-hr. instead of the joule.

A third recommendation is to adopt a unit of thermal resistance. This will save much trouble in calculations of the flow of heat thru bodies and in the transmission of heat in general, as in electric furnaces. Heretofore no unit has existed; the nearest approaches are a number of made-up units for the reciprocal quantity, thermal conductance, such as gram calorie per second per degree, B. T. U. per minute per degree, etc. There are at least 54 such possible composite units of thermal conductance and therefore an equal number for resistance, and

some writers seem to take special delight in complicating matters by inventing new ones, different from the others.

Hence the only way to hope to obtain uniformity and general practice is to combine on a unit which is as rational as possible, is international, and which simplifies calculations as much as possible. The former is accomplished by making it a decimal multiple of the absolute unit, and the latter by choosing that decimal multiple so as to avoid even a decimal conversion factor as much as possible. Moreover, for probably by far the larger number of problems it is simpler to use resistances than conductances, hence it is better to define the unit of resistance and let the other be its reciprocal.

All the above are accomplished by a new unit of thermal resistance proposed by the writer some time ago and called the thermal ohm, a name originally proposed by Dr. A. E. Kennelly, but for a unit of a different magnitude. If the Centigrade degree may be said to be one of the absolute units, then the absolute unit of thermal resistance is that resistance which will permit an erg of thermal energy to be transmitted per second when the difference of temperature is one Centigrade degree. The thermal ohm is made one-ten-millionth of this, hence it is that resistance which will allow one watt of heat current to flow when the difference of temperature is one Centigrade degree.

If thermal resistances are expressed and measured by this unit, then the fundamental law of heat flow is exactly analogous to Ohm's law for electric flow; that is, if the flow of transmission of energy W is in watts, the temperature T in Centigrade degrees, and the resistance R in thermal ohms, then $W = T/R$; that is, the conversion factor then becomes unity, as it does in Ohm's law.

For the few cases in which it may be preferable to use thermal conductances instead of resistances, the reciprocal of this value is recommended, and in order to conform with electric practice, it is proposed to call this the thermal mho.

A fourth recommendation is to urge the use of the Centigrade temperature scale to the entire exclusion of the Fahrenheit scale. It is much more international, and is the one used in the best tables of data. We are making ourselves entirely unnecessary and useless trouble by the use of the Fahrenheit scale.

Many of the engineering calculations are of such a nature that the original data, like those found in tables, could be reduced at the start and once for all to these simpler units, all subsequent calculations, which are by far the more numerous, being then made in the simplified system. The end results may then be converted back into the older system if necessary.

For some classes of specific problems involving a very limited range, the older units may be about as simple to use as the newer ones, but the electrochemist has to deal with an intermingling of at least four forms of energy, electrical, thermal, chemical and physical (change of state), as also with the generation, transmission and consumption of energy in as many different forms, including also its transmission by radiation, conduction and convection, and it is therefore the electrochemical and electrothermal engineer who would be most benefited by the simplifications suggested in this paper.

The chief conversion factors to and from this simplified system are as follows; for others, see the writer's Conversion Tables and some of the papers mentioned below:

Power:

1 watt = 0.238882 gram calorie per second.
1 gram calorie per second = 4.18617 watts.
1 watt = 0.0568776 B. T. U. per minute.
1 B. T. U. per minute = 17.5816 watts.
1 kilowatt = 14.3329 kilogram calories per minute.
1 kilogram calorie per minute = 0.0697695 kilowatt.

Energy:

1 watt-hour = 0.859975 kilogram calorie.
1 kilogram calorie = 1.16282 watt-hours.
1 watt-hour = 3.41266 B. T. U.
1 B. T. U. = 0.293027 watt-hour.

Thermal Resistance:

1 thermal ohm = 4.18617 gram calorie units of resistance.
1 gram calorie unit of resistance = 0.238882 thermal ohm.
1 gram calorie unit of resistance = reciprocal of gram calorie unit of conductance.
(A gram calorie unit of conductance is a conductance which permits a flow of 1 gram calorie per second per degree.)

Thermal Resistivity:

1 thermal ohm, cm. cb. unit = 4.18617 gram cal., cm. cb. units.
1 gram calorie, cm. cb. unit = 0.238882 thermal ohm, cm. cb. unit.
1 thermal ohm, inch cb. unit = 2.54001 thermal ohm, cm. cb. units.
1 gram calorie, inch cb. unit = 2.54001 gram cal., cm. cb. units.
To reduce thermal conductivities given in B. T.U. per hour, per sq. foot, per inch thickness, per Fahrenheit degree, to thermal ohm, inch cube units, multiply the reciprocal of that number by 273.013; or by 693.455 to reduce to cm. cb. units.

In the following papers and articles the writer has discussed this subject of simplified units more in detail:

In *Metallurgical & Chemical Eng.*, Jan., 1911, p. 13, an article on "Thermal Resistance and Conductance; the Thermal Ohm and Thermal Mho," which includes a discussion of these thermal units and a table of conversion factors; it also illustrates their application. The same journal, December, 1911, p. 653, contains a compiled table of thermal resistivities of numerous substances; the January, 1912, issue, p. 43, contains a compiled table of surface resistances. *The Jour. Frank. Inst.*, February, 1911, p. 129, contains an article on "Simplicity in the Measures of Physical Quantities," and the issue of December, 1911, p. 569, one on "Simplifying Some Thermal Calculations by the Use of the Thermal Ohm."

Philadelphia, Pa.

DISCUSSION.

MR. MARTIN L. GRIFFIN: I very much appreciate the importance of saving mental energy. There is one question I would like to ask the author of the paper; namely, where a water power company furnishes power by means of a head and flowage of water, and a customer puts in water wheels, how would you measure the water power in kilowatts delivered to the consumer, where now, perhaps, the power company charges on a basis of so many cubic feet per second, taking into account the varying head, etc.?

I appreciate that there comes in the question of efficiency of the wheels installed, but this is a matter for the customer to provide for.

DR. CARL HERING: The paper dealt with electrochemical calculations rather than with those of mechanics, but I think that even in such a case as that described it would be well to reduce the data to kilowatts at the start, thereby simplifying all further calculations; at least when, as is usual, such water powers are used to produce electric power. I will deduce the conversion factors

required for such reductions to the simplified system, and will give them in my closing remarks.

DR. J. W. RICHARDS: Mr. Hering has been using the thermal ohm per inch cube in a number of his communications, and the possible effect of this was displayed in one or two papers which were sent in for presentation at this meeting. One member measuring thermal resistivities took all his measurements in inches, and did not even express his results in thermal ohms per centimeter cube. It was therefore the duty of the secretary and his assistant to transpose that matter into thermal ohms per centimeter cube, in accordance with the directions of our Board. We should be consistent and use absolute c. g. s. or metric units, or at least use them with the English measures.

DR. HERING: In my papers I generally gave the values in both units. The conversion factors for both are given in this paper, hence there is no inconsistency in this table.

As to using the inch instead of the centimeter, I agree entirely with Prof. Richards that the centimeter would be preferable, and I would much rather use it entirely, but I know that it does not appeal to a great many readers and so-called practical men, and I have therefore tried to adopt the rule to give both in all my writings. I think I have consistently done so, with one exception, and that was simply because the width of the column in the particular journal in which they were published did not permit of another column of figures.

PRESIDENT WHITNEY: This matter of the introduction of the metric system is gaining ground steadily. I do not think anyone expects to go into a manufacturing plant and have them discard entirely the present English system. You cannot change to the metric system at once, but it must be apparent that by adding the equivalents in the metric system to the figures given in this paper we are making a decided advance towards the more general adoption of that system.

MR. MARTIN L. GRIFFIN (*Communicated*): Since power is one of the fundamental factors which the electrochemist deals with in his work, and since he is concerned with a great variety of forms of energy, it is very important that all units of measure-

ment should be simplified as far as possible and be brought into one comprehensive system. In this work of simplification, Dr. Carl Hering is a pioneer. As in the case of educating the public to change from the old system of English weights and measures to the metric system, so it will be an educational process to bring into one comprehensive, rational system the heterogeneous units of energy.

Flowing water will continue to be an increasing source of electrical power, and it is important that the use of the antiquated horse-power should be supplanted by a metric electrical unit, the value of which can always be determined and about which there can be no misconception as to its value. Originally the horse-power was derived from the estimated work a horse could do, and this was determined by observing the performance of the horse under varying conditions. Of course no uniformity could be expected, and finally an arbitrary standard of rate of work was fixed as the horse-power. The ox or ass might have been chosen to represent the unit with equal propriety.

There are so many analogies between the flowing stream of water and the flowing electric current that it becomes a very easy task to express each in terms of a common unit. The elements of energy are potential, volume and a constant time differential. The elements of water-power are commonly expressed by the head and flowage rate, often as feet and cubic feet, more rarely as meters and cubic meters. The elements of electric energy are expressed by the corresponding terms—voltage and amperes. There is therefore no good reason why the energy of a falling body of water should not be measured by the same unit used in the measurement of electrical energy, namely, the watt or kilowatt. This analogy is not necessary to justify the use of the kilowatt in mechanical measurements, for it is defined purely mechanically, and not electrically at all. That it is used generally in electrical work is merely accidental, due to its convenience as a metric unit, and to fit in naturally with the metric units in which all electrical quantities are universally expressed.

The kilowatt is defined in purely mechanical terms as follows: "The kilowatt is the power developed by the action of a force with a velocity of one meter per second, which force is capable of giving to a mass of one kilogram in one second a velocity

of one kilometer per second." The power rate delivered by a stream of water can be determined in kilowatts by multiplying the factor 0.163 into the product of the head in meters by the flow in cubic meters per minute. The total energy delivered during a period of time may be expressed in kilowatts by multiplying the rate in kilowatts by the time in hours. Where, therefore, engineers have been in the habit of computing water-power in terms of the old English units of cubic feet per second, they would aid the cause by changing to the metric system and substituting the kilowatts for the horse-power.

DR. HERING (*Communicated*) : The conversion factors inquired about by Mr. Griffin in his remarks at the meeting are as follows:

Hydraulic power is stated in terms of the product of the height of the fall by the rate of flow of the water, hence in terms of feet $\times$ cubic feet per second, or meters $\times$ cubic meters per second. This product must then be multiplied by the weight of a cubic foot or a cubic meter of water, and then by another factor to reduce it to horse-power; hence it certainly involves no more work to simply use a different multiplier to reduce it directly to the more rational power unit, the kilowatt, and it saves calculations thereafter if the water-power is to be used for generating electrical energy, as is usually the case.

If the numerical product of the feet fall and the cubic feet per second is designated in "water-power units," and that in meters fall and cubic meters per second in "metric water-power units," then, on the basis that one cubic decimeter of water weighs one kilogram, the desired conversion factors for direct reduction, to and from the rational system, are:

1 water-power unit	=	0.0846357 kilowatt.
1 metric water-power unit	=	9.80597 kilowatts.
1 kilowatt	=	11.8153 water-power units.
1 kilowatt	=	0.101979 metric water-power unit.

Hence for approximate calculations, dividing the product (feet fall $\times$ cubic feet per second) by 12 gives the kilowatts (error less than 2 percent). Or multiplying the product (meters fall $\times$ cubic meters per second) by 10 gives the kilowatts (error slightly over 2 percent).

Replying now to Mr. Griffin's communicated remarks, I call attention to the fact that although there are many analogies between a current of water and a current of electricity, yet there are no possible equivalents between the height or pressure of water and volts, as they are totally different physical quantities; the same is true of the quantity of water flowing and the quantity of electricity flowing. But when both flows are reduced to their energy, then there are very definite equivalents between them, as energy is common to both.

Mr. Griffin's point is well taken when he states that the kilowatt may be defined in purely mechanical terms, showing that it is really a mechanical unit based on the absolute or c. g. s. system; it is applied to electrical energy simply because the electrical units are based on that system.

I would suggest that the definition of the kilowatt, which he quotes, might perhaps be more readily understood if stated as follows:

A kilowatt is that power which is developed by a certain force acting at the rate of a meter per second, this force being equal to one which, if acting on a mass if one kilogram for one second, would produce a velocity of one kilometer per second. Numerically this force in question is therefore equal to 10^8 dynes, or to 101.979 kilograms, or 224.825 pounds.

The unfortunate fact that this is an odd number of kilograms is due to the dyne and the gram being incommensurate, as they are connected by the acceleration of gravity, which is a terrestrial constant.

In the simple and rational system of units the falling water in a water-power should be considered as a force, which, in fact, is really what it is when it generates power. The c. g. s. unit of force is a dyne, but as this is inconveniently small the practical unit is taken to be a million times this and is called a megadyne (equal to 1.01979 klg. or 2.24825 lbs.). Now, a kilowatt of power is equal to a force of 100 megadynes acting with a velocity of one meter per second, or, in general,

$$1 \text{ kilowatt} = 100 \text{ (megadynes} \times \text{meters per second)}$$

$$1 \text{ (megadyne} \times \text{meters per second)} = 0.01 \text{ kilowatt}$$

in which it will be seen that the numerical conversion factor becomes just 100, hence virtually drops out of the calculation.

If therefore our reference books would tell us, as they should, that a cubic meter of water exerts a true force of 980.597 megadynes, then, after converting the cubic meters to units of force, the rest of the calculation will be free from conversion factors. One megadyne of force is produced by 0.00101979 cubic meter of water.

It may be said that this merely shifts the incommensurate conversion factor to another place in the calculation. This is true in this particular case, but if it can thus be shifted it is often possible to shift it still further back into the original data (say, into the gaugings in this case) where it enters only once, or into the tabulated values of constants, and it is thereby disposed of, so that the numerous subsequent engineering calculations may be made in the simple system. In general it is advisable to reduce the original data at once to the simplified units so that all the more numerous subsequent calculations may be made in the simple system.

The following constants may sometimes be of use, and are given here to complete the set:

POWER.

General:

1 watt = 10,000,000 ergs per second.

Mechanical:

1 gram-centimeter per second = 0.000,098,059,7 watt.
1 foot-pound per second = 1.355,73 watts.
1 kilogram-meter per second = 9.805,97 watts.
1 megadyne-meter per second = 10 watts.
1 kilowatt = 100 megadyne-meters per second.
1 metric horse-power = 0.735,448 kilowatt.
1 horse-power = 0.745,650 kilowatt.

Thermal, chemical, physical, etc.:

1 pound-centigrade heat unit per minute = 31.646,9 watts.

FORCE.

1 dyne = 1.019,79 milligrams.
1 megadyne = 1,000,000 dynes.
1 gram = 980.597 dynes.
1 pound = 0.444,791 megadyne.
1 kilogram = 0.980,597 megadyne.
1 cubic foot of water (downward force) = 27.767,6 megadynes.
1 cubic meter of water (downward force) = 980.597 megadynes.

ENERGY.

General:

1 erg = 1 dyne-centimeter.
1 watt-second = 10,000,000 ergs or dyne-centimeters.
1 watt-hour = energy of 10,000,000 ergs per second during one hour.

Mechanical:

1 gram-centimeter = 980.596,6 ergs.
1 foot-pound = 0.000,376,591 watt-hour.
1 kilogram-meter = 0.002,723,88 watt-hour.
1 megadyne-meter = 10 watt seconds.
1 (feet fall × cubic feet of water) = 0.023,509,9 watt-hour.
1 (meter fall × cubic meters of water) = 2.723,88 watt-hours.

Thermal, chemical, physical, etc.:

1 gram calorie = 4.186,17 watt-seconds or 0.001,162,82 watt-hour.
1 pound-centigrade heat unit = 0.527,448 watt-hour.

PRESSURE.

1 barie = 1 dyne per square centimeter.
1 megadyne per sq. cm. = 1 megabarie.
1 megabarie = 1,000,000 baries.
1 gram per square centimeter = 980.597 dynes per sq. cm.
1 millimeter of mercury column = 1,333.21 dynes per sq. cm.
1 foot of water column = 0.029,888,6 megadyne per sq. cm.
1 inch of mercury column = 0.033,863,7 megadyne per sq. cm.
1 pound per square inch = 0.068,942,5 megadyne per sq. cm.
1 meter of water column = 0.098,059,7 megadyne per sq. cm.
1 kilogram per square centimeter = 0.980,597 megadyne per sq. cm.
1 atmosphere (760 mm. Hg.) = 1.013,24 megadynes per sq. cm. (megabaries.)

THERMAL RESISTANCE.

Thermal ohms = centigrade degrees ÷ watts = degrees per watt.
1 thermal ohm = a resistance requiring 1°C per watt of heat flow.
1 thermal ohm = 0.000,000,1 c.g.s. unit of thermal resistance.
1 gram calorie unit = a resistance requiring 1°C per flow of 1 gram calorie per second.
1 c.g.s. unit = a resistance requiring 1°C per flow of 1 erg per second.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

EFFECTS OF THE VARIATIONS OF THERMAL RESISTIVITIES WITH THE TEMPERATURE.

By Carl Hering.

In a paper read before this Society several years ago[1] the writer published the rigidly correct formulas for calculating the heat loss thru thick furnace walls in which the flare becomes great, and showed the effects produced by varying the thickness. In that analysis the temperature gradients in such walls were not included, and for simplification it was assumed that for the walls as a whole the thermal conductivity or resistivity of the material was represented by its correct mean value over the whole range of temperature.

As the ranges of temperature in electric furnace walls may be very great, the variations of the resistivities of the material may become quite appreciable, as also the resulting effect upon the distribution of the temperatures as represented by the temperature-gradients.

The purpose of the present paper is to discuss the effects which are produced by these temperature variations of the thermal resistivities, and to show how the correct mean values may be determined under certain conditions.

To do this, some law of variation of resistivities must be assumed. Knowledge on this subject is very meager; the only fact which seems to be known definitely is that the resistivities of refractory materials become smaller as the temperatures become greater. Nusselt,[2] who has recently made some apparently very good determinations of the thermal conductivities of a few materials, comes to the conclusion that in general the thermal conductivity of such materials increases at the rate of 1/273 part for every degree centigrade above 0°C. He does not give this

[1] Heat Conductance Through Walls of Furnaces. These Transactions, **14**, 215 (1908).

[2] Zeit. Ver. Deut. Ing., June 1908, p. 906.

as a well established law, but merely as an approximate result of his tests. This would mean that the thermal conductivity increases according to a straight line law and in proportion to the absolute temperature, as shown by the straight line in Fig. 1 for fire brick on the basis that at 1000°C. its resistivity is about 25 thermal ohms. The conductivity is therefore zero at absolute zero, that is, the material is then a perfect insulator (when no heat exists). Altho this law may not be strictly correct, it seems

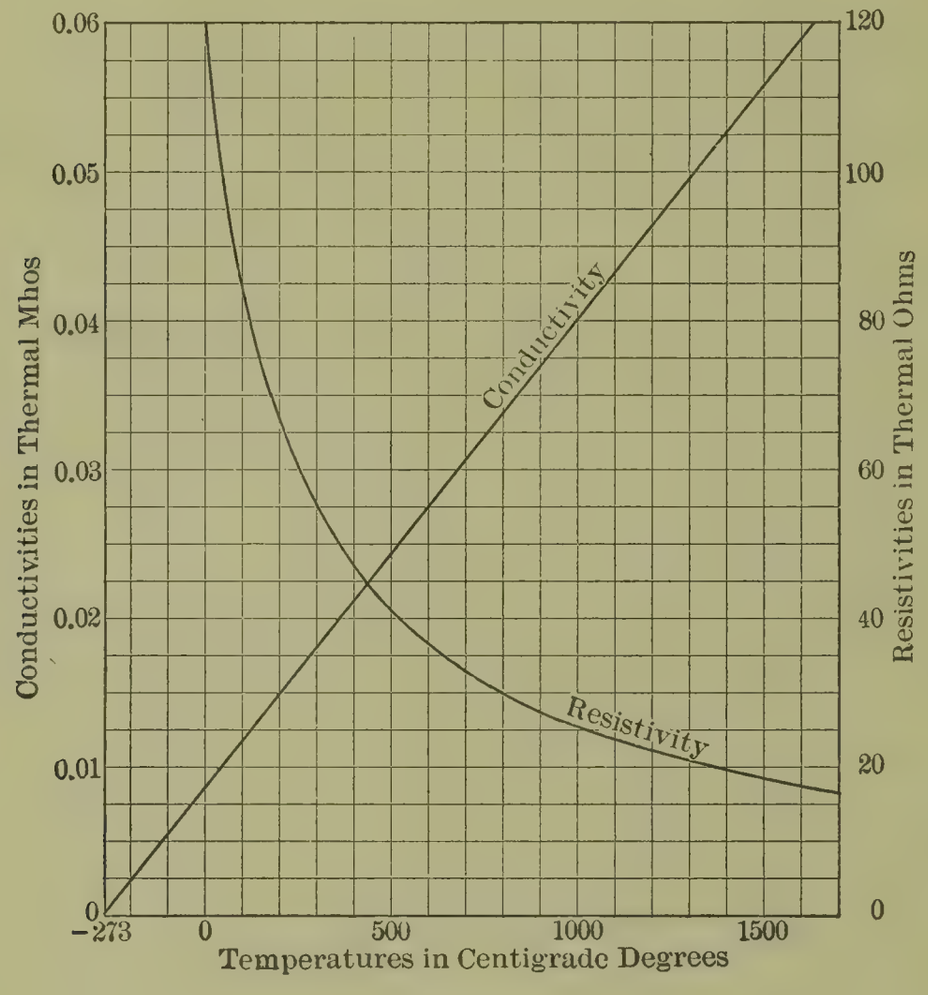


FIG. 1.

to be the only one existing, and as it appears to be a rational one and is probably not far wrong at the usual temperatures, it will at least take us a step nearer than no law at all. The deductions below will be based on this law.

Quantitatively this corresponds approximately with the variations in the electrical resistivity (not conductivity) of copper and other pure metals, which are also said to be zero at the absolute zero. Hence the relative variation is not as great as might at first appear, but the actual variations become large

because the ranges of temperature are generally quite great. For instance, according to this law the thermal conductivity at 273°C. is double that at 0°, at 546°C. it is three times, at 819°C. four times, at 1092°C. five times, at 1365°C. six times, and at 1638°C. seven times, etc.

If T is the temperature on the absolute scale, and k the conductivity in reciprocal thermal ohms[3] (thermal mhos) then the formula for any temperature is

$$k = aT \tag{1}$$

in which a is a constant for each material; for fire brick for instance it seems that a is equal roughly to about 0.000031 when k is in inch-cube units.

Or put into the more usual tho more cumbersome form

$$k_t = k_o (1 + at) \tag{2}$$

in which k is in the same units as before, but t is now in centigrade degrees, and a is a different constant; then for fire brick

$$k_t = 0.0086 (1 + 0.0037t) \tag{3}$$

k being again in inch-cube units.

For resistivities the law is then no longer a straight line law but a hyperbolic one, as shown for fire brick by the curved line in Fig. 1. The simplest formula then is

$$r = \frac{b}{T} \tag{4}$$

in which r is the resistivity in thermal ohms, T is the absolute temperature, and b a constant (equal to the reciprocal of a in (1) for k); or if t is the temperature in centigrade degrees, then

$$r = \frac{b}{t + 273} \tag{5}$$

For fire brick b seems to be equal roughly to about 32000, when r is in thermal ohm, inch cube units.

On the basis of this law the respective constants a and b for any material can be readily determined from a table of resistivities such as the one published by the writer in Met. & Chem. Eng.,

[3] The Thermal Ohm and Thermal Mho, Met. & Chem. Eng., Jan., 1911, p. 13.

Dec. 1911, p. 653, when the values are given for any specific temperature; if, however, a value is given as a mean for a given range of temperature, then it can be shown that it is also the value for a temperature midway between the two extremes of that range. If, for instance, the resistivity of fire brick is given as 23 thermal ohms for one inch cube, for a range from 500° to 1300°C., then that is also its value at 900°. This will be demonstrated below.

Having now assumed a law of variation, it becomes possible

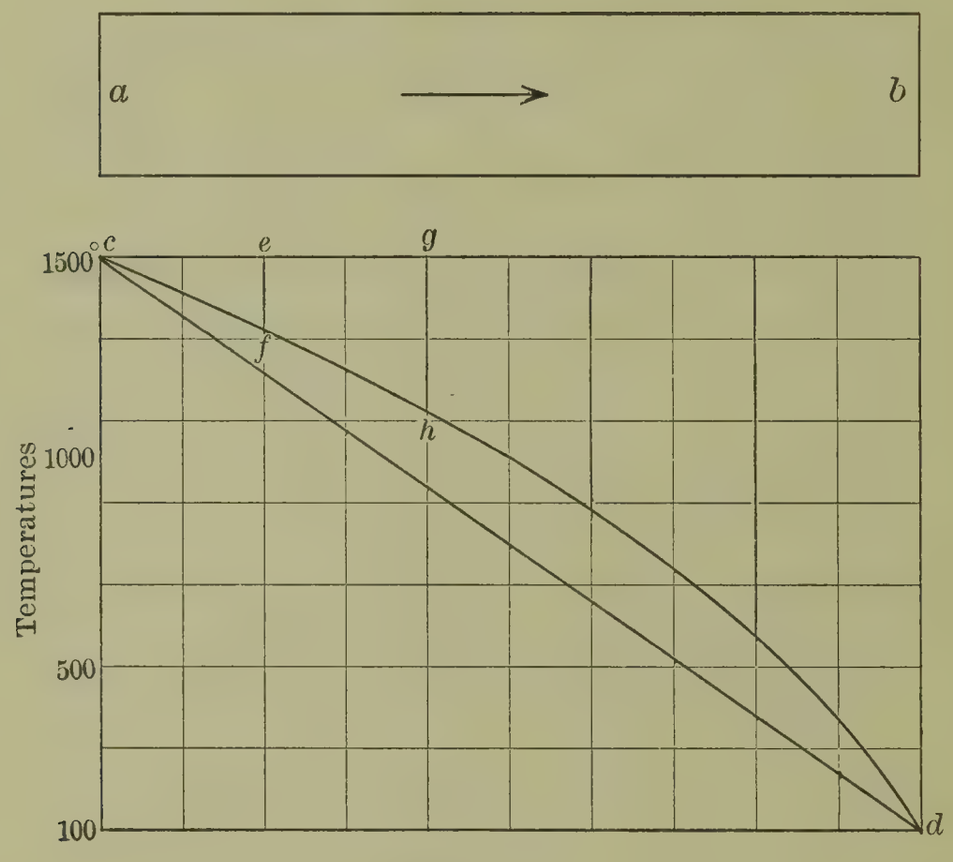


FIG. 2.

to determine the heat gradients in conductors thru which heat is flowing, hence the temperatures at different parts. Altho the results involve the same inaccuracies as those of that law, they are unquestionably far closer to the correct ones than if a constant mean value be assumed thruout.

Let *ab* Fig. 2 be a cylindrical or prismatic rod thru which heat is flowing from *a* to *b*, and assume that none is lost thru the sides. If the mean value of the resistivity were taken to be constant from end to end, the heat gradient would be the straight line *cd* shown in the diagram below it, no matter what the

resistivity, temperatures or quantity of flow, except that the scale may differ.

But as the resistivity is known to be lower at the higher temperature it follows that the correct gradient will be less steep at the hot end and steeper at the cold end, as shown in the curve *cd*. This curve can be drawn by means of several trial calculations. Assume for instance the rod be divided into five successive sections. For the first approximation take the temperatures in the middle of each of these parts, from the straight line gradient, which is only approximately correct. Then for each of these find the resistivity corresponding to that temperature, say by means of formula (4), not forgetting to add 273° to each to reduce to the absolute scale, and taking care to distinguish between a drop of temperature and an actual temperature. With these new resistivities calculate the corrected resistance of each of these five sections; they will now all be different, the hotter ones having a smaller resistance. Add them to get the total, from which and the thermal Ohm's law, watts = temperature ÷ resistance, find the flow of heat which will give the same total drop. With this flow and the resistance of the first section find the drop of temperature thru that section ($T = WR$) and lay it off as *ef* at the end of the first section. Then determine the drop thru the second section, add it to the first and lay off as *gh*, and so on to the end *b*. The curve thru these points then gives the second approximation. By then taking the temperatures from this curve and repeating the calculations, gives a third and still closer approximation to the true temperature gradient, probably amply sufficient for most purposes. It is an integration curve, the ordinates of which (measured downward from above) are equal to the total resistances from the beginning to each particular point. It could also be determined algebraically.

From this corrected heat gradient it will be seen that the higher temperatures penetrate much farther into the rod than with a constant resistivity. The temperature in the middle will be far higher than the mean of the two at the ends, and the average will also be higher, hence the total insulation resistance will be less than the arithmetical mean value between the two resistivities

at the ends would give. It would therefore give too high a resistance if such a mean value were used in calculations.

When such a curve is correctly drawn, the true mean value of the resistivity may be determined from it, by getting the sum of the resistances of all the five individual sections, multiplying by the cross section and dividing by the length. If then this value be compared with the curve of resistivities in Fig. 1 for that material, it will be found to be the one for the temperature midway between the extremes.

As an actual illustration, assume fire brick as the insulating material. Let (4) be used to determine the resistivities. Let the constant b be 32,000 for inch units. Let the hot temperature be 1,500°C. and the cold one 100°, this latter temperature being assumed to be kept constant, say by water cooling, so as not to complicate the present problem by the introduction of still further variables; when there are numerous variable factors all affecting the final result, the writer considers it better to take up the effect of each one separately and independently of the others, and combine them later after the effects of each of the individual ones have been determined.

By drawing the curve as just described, and then finding from it what the true mean value for fire brick is, it will be found to be 29.8 thermal ohms for one inch cube. That at the higher temperature will be 18.0 and at the lower 85.7, the mean of which is 51.8 which will be seen to be far too high, it being in error by 74 percent. It is therefore only a very crude approximation to take as a mean value the arithmetic mean between the two extremes; the geometric mean is also wrong, altho much nearer to the correct value. It will be found from (4) that the correct mean value 29.8 is that for 800° in this case, and this temperature is the mean between the two extremes 1,500 and 100.

Hence the correct rule when dealing with resistivities, is to take the mean of the two temperatures and find the resistivity for that mean temperature, this will then be the correct mean value to use. This is rigidly correct under the assumptions, one of which is the law of variation stated above. The algebraic proof will be given below.

When conductivities are used instead of resistivities, the same rule applies; but as the law of variation is then a straight line

law, it is also correct to take the arithmetic mean of the conductivities at the two extreme temperatures.

In the above it was assumed for simplicity sake, that the conductor had the same cross section thruout; in most cases of thermal insulation, however, the conductor flares and often quite considerably.

Let the upper part of Fig. 3 represent such a flaring conductor.

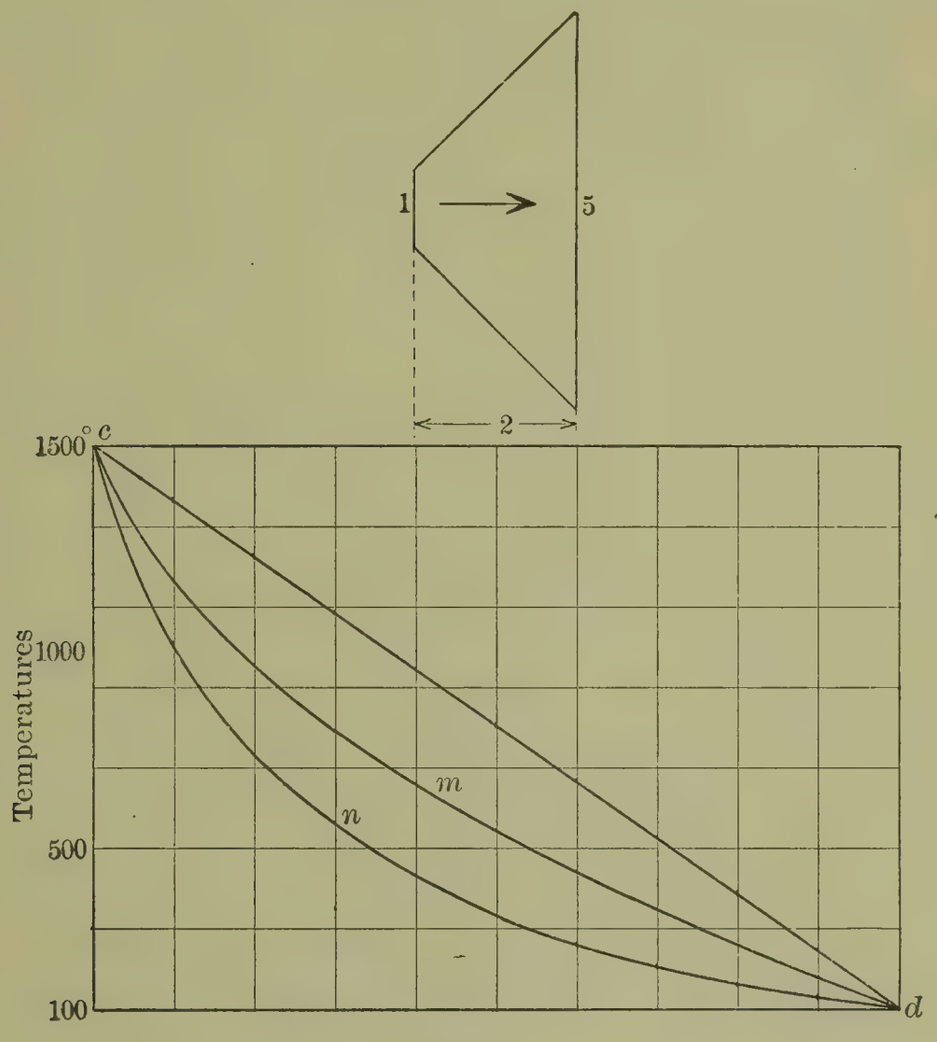


FIG. 3.

somewhat exaggerated in wall thickness in order to show the effect of the flare more clearly; the thickness is here taken as twice the inside dimension of the furnace. Let it be one of the six sides of a cubical furnace, or an element of a spherical one, or in general, one in which the cross section (perpendicular to the flow) increases as the square of the distance from the geometric apex.

At first assume a constant resistivity and proceed as above described by dividing the conductor into sections and determin-

ing the resistance and drop of temperature in each section; the mean cross section of such a flaring conductor, as also that of each of the sections, is the square root of the product of the two end surfaces, that is, their geometric mean.

This will give as the heat gradient, the curve *cnd;* this corresponds to the straight line in Fig. 2, and again is the same for all resistivities, flows and temperature drops, differing only in the scales. According to this curve *cnd,* the temperature falls very rapidly at the hot side, and very slowly at the cold side. The temperature drops to one-half at only one-sixth of the distance from the inside surface, and at half the distance it has dropped to as much as one-sixth of the total. It would therefore appear from this first approximation that the outer layers are almost useless for insulation.

By correcting this curve for the variations of the resistivities by temperature, as described above, and obtaining a second and third approximation, the curve *cmd* will be obtained; this corresponds to the curved gradient in Fig. 2. In comparison with *cnd* this shows that the temperatures drop less rapidly at first than before, and that they drop faster in the outer layers than before; the curve, in fact, approaches toward the straight diagonal line *cd* which would represent a case in which every inch of thickness has the same insulation value; roughly, the curve *cmd* is about half way between *cnd* and this straight line.

This corrected curve *cmd* shows that, owing to the change of resistivity with the temperature, the higher temperatures penetrate considerably more deeply into the wall, at first about twice as deep. The first half of the temperature drop now occurs at about one-third the distance from the inside wall, and in the middle of the wall it has now dropped to only about a third of the total.

One of the important deductions from this is that the outside layers of even this exceptionally thick wall are of considerably greater value as insulators than might at first be supposed. This is due to the fact that the resistivity of the colder layers increases so much that it tends to balance the effects of the increasing cross-sections; it does not equal them, altho it comes about half way toward doing so.

Having obtained this corrected curve, say, for fire brick, and

for the same temperatures and constants as before, the correct mean value can be determined. In the present case this will again be found to be 29.8 thermal ohms for fire brick, the same as for the straight bar without a flare. It follows therefore that all that was said above concerning the correct mean applies to such flaring conductors as well.

Hence the correct mean value to use for the resistivity of a flaring wall is the resistivity corresponding to the mean temperature and not the mean of the two extreme resistivities. An algebraic proof of this will be given below.

As the resistivity for the mean temperature is considerably less than the arithmetic mean of the resistivities at the two ends, the insulation will be considerably lower than if based on the latter mean, hence it is important to make this correction. On the other hand, however, when such constants were originally determined experimentally, it may have been that the cooler temperature was considerably greater than that of the outside wall of a furnace for which they are applied. In that case the mean resistivity found from the tests is too low to be applied directly to such a furnace wall; the actual insulation of a wall would then be higher (better) than the one calculated from such a value, unless it was first corrected as will be described.

The above deductions had therefore better be applied to the experimental determinations also, thus obtaining a single value for each material, as for instance the constant b in formula (4), and there can then arise no error in applying it to different ranges, except of course any error there may be in the assumed law of variation; but even such an error will be in part eliminated when this same law is used for deducing the constant and then afterwards used for applying it; such a double or reversed use of an approximate law tends to diminish the error in the law, and if such a double use enables one to get closer to the desired result than no law at all, the net result is a gain, even tho it is not precise.

Hence if in a determination of a constant the range of temperature was say 400° to 1200°, then the value obtained should be taken as that for $(400 + 1200) \div 2 = 800°$. Adding 273° and applying formula (4) gives the constant b, which result can then be applied to any other temperature. The quantity b is

the resistivity that the material would have from 0° to 1° absolute temperature.

Analytical. Altho the above results, which are rigidly correct on the basis of that law, are nearly self-evident, it may be of interest to give the mathematical proof, as it might be desired to apply the general method of proof to some other law.

The law being simpler for conductivities than for resistivities, it is better to use the former.

Let T and T′, Fig. 4, be the absolute temperatures at the two ends of a cylindrical rod of uniform section S, and length L, and let a quantity of heat H enter at T and leave at T' without

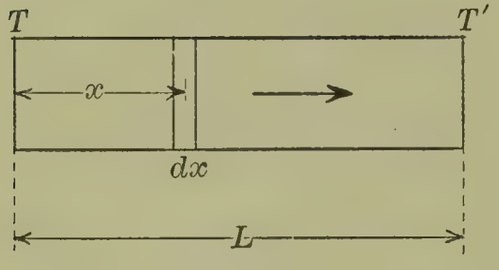


FIG. 4.

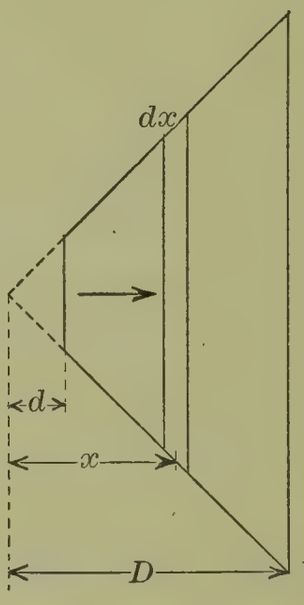


FIG. 5.

loss thru the sides. Let k be the variable conductivity and K its desired mean value. Let dx represent an infinitely small sectional element at a distance x from the hot end; and let t be the temperature at that distance x.

The heat flowing thru this section will then be

$$H = - kS \frac{dt}{dx} \qquad (6)$$

This is constant by definition and is equal to that thru the rod as a whole, namely,

$$H = \frac{KS\,(T-T')}{L} \qquad (7)$$

According to the assumed law

$$k = at \tag{8}$$

in which a is the physical constant of any particular material (namely, its conductivity from 0° to 1° absolute temperature). Substituting this value of k in (6), placing (6) equal to (7) and reducing, gives

$$-tdt = \frac{K(T-T')}{aL}\,dx \tag{9}$$

Integrating the left hand side between the limits T and T', and the right hand side between the limits zero and L, gives

$$\frac{T^2-T'^2}{2} = \frac{K(T-T')}{a} \tag{10}$$

which reduces to

$$K = \tfrac{1}{2}a(T + T') \tag{11}$$

Comparing this with (1) shows that this correct mean conductivity K is that for the mean of the two temperatures. And as the resistivity is always the reciprocal of the conductivity, it follows that the correct mean resistivity is also that for the mean of the two temperatures. Altho absolute temperatures were used in the above, the rule for the mean temperature applies also to ordinary Centigrade degrees, provided that 273° be then added before it is used in formulas (1) or (4).

Equation (11) can also be written

$$K = \tfrac{1}{2}(aT + aT') \tag{12}$$

which means that the mean value K is also equal to the arithmetic mean of the conductivity at T and that at T', because aT and aT' are equal to those two conductivities respectively, according to (1). The corresponding result is, however, not true of the resistivities, because the law is then no longer a straight line law.

To give a similar analytical proof for a flaring conductor, let Fig. 5 represent such a conductor and let its flare be such that the section increases as the square of its distance from the apex, as is the case with the elements of cubical or spherical shells. Let d and D represent the distances of the two end surfaces

from the apex, hence $D - d = L$; and let s and S represent the small and large end surfaces respectively; hence the proper mean cross-section is the square root of $s \times S$.

Equation (6) will be the same except that the cross-section S in that formula now becomes a variable, and according to the above assumption it is equal to

$$sx^2/d^2 \tag{13}$$

Hence

$$H = -\frac{ksx^2}{d^2}\frac{dt}{dx} \tag{14}$$

Equation (7) now becomes

$$H = \frac{K(T-T')\sqrt{Ss}}{D-d} \tag{15}$$

Substituting $k = a\ t$ as before, equating (14) and (15) and reducing, gives

$$-tdt = A\ dx/x^2 \tag{16}$$

in which A contains all the constant factors not concerned in the integration. Integrating the left hand side between the limits T and T', and the right hand side between the limits d and D, gives

$$1/2(T^2-T'^2) = A(1/d - 1/D) \tag{17}$$

The value of A was

$$A = \frac{d^2\ K\ (T-T')\ \sqrt{Ss}}{as\ (D-d)} \tag{18}$$

Substituting this and reducing, remembering that the ratio of the surfaces S and s is equal to the ratio of the squares of D and d, gives

$$K = \tfrac{1}{2}a(T + T') \tag{19}$$

which is the same as (11).

Hence what was said above concerning conductors of uniform section applies also to flaring bodies like those forming hollow cubes or spheres.

Conclusions. The conclusions of the above analysis, based on the assumption that the thermal conductivity increases in proportion to the absolute temperature, are briefly as follows:

The proper mean value of the thermal resistivity or conductivity for the conductor as a whole, is the value for the mean of the two extreme temperatures. The mean of the two extreme values of the resistivity would give a far too high resistance; but for conductivities this mean is correct.

This applies not only to conductors of uniform section, but also to those that flare like the parts of cubical or spherical shells.

The formula for calculating the resistivity for any temperature is (4) or (5), and for conductivity (1).

The variations of resistivity and conductivity are shown in Fig. 1.

The correct heat gradient in a conductor of uniform section is shown by the curved line in Fig. 2, and for a flaring conductor by *cmd* in Fig. 3.

Addendum. Since the above was written, Dr. Horace Clark Richards, of the University of Pennsylvania, has carried the proof still farther and finds that this law is a much more general one. In a communication received after the above was written, he summarizes his results briefly as follows:

"I find that the interesting results which you obtained for the thermal resistance of a conductor, in which the conductivity varies as the absolute temperature, are special cases of a more general law. My conclusions may be summarized as follows:

"(1) The correct value of the equivalent constant conductivity to use in calculating the resistance of a conductor is the arithmetical mean of its values at the ends, not only for the cases of uniform section and uniform spherical (or cubical) flare, as you found, but for a conductor of any form whatever, provided that the surface, except the ends, is insulated.

"(2) The same law is applicable when the conductivity is *any* linear function of the temperature, as $k = k_0 + at$, and therefore is the correct approximation when the law is not more exactly known.

"(3) In general, when the conductivity varies with the temperature according to any law, the equivalent conductivity of the

conductor is the temperature-average of its conductivities, *i. e.*, if a curve is plotted with temperatures as abscissas and conductivities as ordinates, the proper value is the average ordinate of the curve. This could be obtained by a plantimeter or by Simpson's rules, etc., if necessary, or, if the law can be exprest mathematically, by the formula:

$$k' = \frac{1}{t_2 - t_1} \int k \, dt$$

where k is the conductivity at any temperature t; t_1 and t_2 are the temperatures at the ends, and k' the equivalent conductivity.

"Of course it is obvious that all this applies equally to electrical conductivity."

Philadelphia, Pa.,
January, 1912.

DISCUSSION.

Mr. F. A. J. FitzGerald: Mr. Hering's paper is interesting and timely, for on the one hand a theoretical discussion of this kind is a useful guide in the designing of furnaces, and on the other the subject of prevention of heat losses is now engrossing the attention of many investigators. Nevertheless it is of great importance in matters of this kind to be very cautious about accepting the mathematical calculations based on theoretical considerations, and to avoid disastrous mistakes by checking the results by experimental work. Some eight years ago it was remarked, in relation to a theoretical discussion of the carborundum furnace:

"Finally, it must be borne in mind that this discussion of the theory of the carborundum furnace cannot be used directly in practice, for on account of the numerous assumptions that had to be made and various factors left out of consideration, the results arrived at are different from those found in the actual furnace. Nevertheless, a study of an ideal furnace of this kind is undoubtedly of help in practice * * *."[1]

[1] "Monographien über angewandte Elektrochemie," XIII Band; "Carborundum," von Francis A. J. FitzGerald, p. 15.

A similar remark applies to the theoretical study of heat losses. An example of the great need of caution in arriving at conclusions based on theoretical considerations, or on experiments which only consider one element of a problem, is to be found in the introduction to Queneau's valuable translation of Wologdine's paper on the heat conductivity of refractory materials.

Queneau writes:

"The great value for heat insulation purposes of silica brick when burned at a moderate temperature, 1050° C., is due to

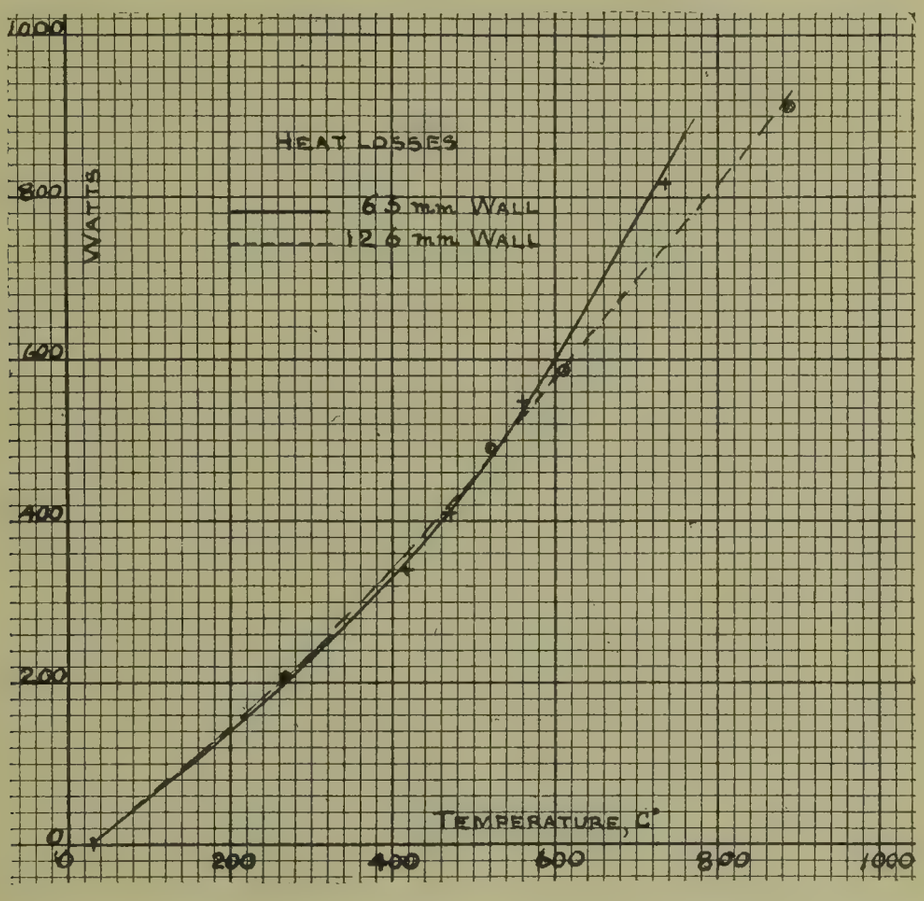


FIG. 6.

the fact that their coefficient of heat conductivity is practically equal to that of Kieselguhr brick and only one-half that of clay brick."

Now it may be that some silica brick are good heat insulators, but it is dangerous to draw such conclusions as regards silica brick in general, as is shown by the paper "Experiments on Heat Insulation" presented at this meeting. An experiment not described in this paper is interesting in its relation to the calculation of heat losses on theoretical grounds.

It would be a natural conclusion that increasing the thickness of the heat insulation of a furnace would diminish the heat losses; but the experiments with the furnace described in the paper mentioned above shows the need for caution in counting on this. The accompanying curves, Fig. 6, show the heat losses corresponding to different furnace temperatures with 63 mm. (2.5 inch) walls (full line curve) and those determined with a 126 mm. (5 inch) wall. It will be observed that until the furnace temperature is above 550° C. there is no appreciable difference in the heat losses.

It must be noted that the conditions of this experiment are complicated. In the case of 63 mm. walls we have a single thickness of brick and that with the 126 mm. walls there are two separate thicknesses of brick, the extra 63 mm. being, so to say, a jacket on the other furnace. In the loss of heat various factors enter in:—radiation, convection and conduction. The radiating surface with the double wall is, of course, much greater than with the single wall. The probability of losses by convection currents through joints in the bricks are less with the double wall. The temperature gradients are, of course, different in the two cases. The conductance is seriously modified in the case of the double wall by the resistance of the surface contact between the inner and outer walls—and so forth.

In view of these complicated conditions it is unsafe to depend on calculations based on our present data, and we must, therefore, depend on experimental results.

It must be clearly understood that these remarks are in no way a detraction from the value of Mr. Hering's paper; but are merely for the purpose of calling attention to the danger in our present state of knowledge of relying on theoretical considerations.

President Whitney: If one man would do the scientific end of such work and another man the experimental end, and both of them follow the work zealously, they would do better work combined than one man could do alone on the two subjects. By having such papers on this subject presented at the meeting we can keep an active interest in the subject. This matter of heat insulation is always going to be considered with masses,

cubical or spherical, of finite dimensions. The use of electrical energy for heating, from heating electrical furnaces to running refrigerators, is also going to come to pass. You have, therefore, the question of insulating everything from zero to 3600° Centigrade, and there is hardly a more important subject that we can touch on than the methods of calculation, and the proving of the calculations by experiment.

Dr. W. Lash Miller: Dr. Hering's result can be deduced briefly from Fourier's equation for the conduction of heat

$$\frac{\partial t}{\partial \theta} = \frac{\partial}{\partial x}\left(k \frac{\partial t}{\partial x}\right)$$

When the stationary state is reached, $\frac{\partial t}{\partial \theta} = 0$, and $\int k dt = x - x_0$. Thus, if k (the conductivity "constant") be independent of the temperature (t)

$$k(t - t_0) = x - x_0$$

while if k be a function of the temperature, a fictitious constant k' may be substituted for the real k by setting

$$k'(t - t_0) = \int k dt$$

as proposed by Hering and H. C. Richards.

Dr. J. W. Richards: I have analyzed the results of Mr. Randolph's paper on heat resistivities with a view to seeing whether they agreed with this law which Mr. Hering has assumed, and I found there was only one material there which agreed closely with it. That was substance No. 108-A, called "Poplox," dried at 500° C. The conductivity of the others increased at less than this rate, down to No. 1018, which practically did not vary in conductivity at all with the temperature.

Mr. FitzGerald: The curves given in my paper, to follow this, show the actual effect of doubling the thickness of furnace walls, and the curves are not exactly what would be expected.

Mr. Hering: Of course, such results as Mr. FitzGerald gives in his curve, Fig. 6, in his paper, do not agree with the law, but if I had gotten such results I should feel that I ought to

look for errors or inconsistencies in the experiments. I certainly should not condemn fundamental laws because such involved experimental results did not correspond with them.

In my opinion, fundamental laws are very useful, both in practical designing and in guiding us in our experiments; I think we ought always to try to have the fundamental laws before us in order to be able to interpret the results of our experiments more rationally, and to guide us in drawing correct conclusions from them.

In his experiments he has apparently combined the internal resistance of the material with the surface resistances. In my opinion it is very much safer and better to try to separate these two resistances, and not to try to get the one law to apply to both, because the laws seem to be different in kind. I should certainly not assume the outside temperature to be that just outside the surface; there may be a very great drop of temperature there. When we measure the temperatures of such surfaces a great deal depends on the correctness of that measurement.

I think that probably the best results could be obtained with graded waxes instead of trying to get the temperature of the surfaces with a thermometer or pyrometer. If one uses such instruments on surfaces of insulating materials they will be sure to cool the little spot which the thermometer touches and therefore will indicate an entirely different temperature there from that which really existed before the thermometer was applied. With graded wax their melting temperatures could first be established very carefully, and one can be sure that these waxes would assume the true temperatures of the surfaces.

In Mr. FitzGerald's experiments it seems that the surface resistance was probably by far the more important of the two, and therefore he gets so little difference between two walls of different thicknesses. The same thing was noticed many years ago when it was first found out that copper conducted heat better than iron, and it was therefore thought that steam boilers should be made of copper instead of iron. Two boilers were therefore constructed exactly alike, one of copper and one of iron; both were tested and it was found that they were equal as to thermal conductivity. The explanation is that the thermal resistance in a steam boiler is almost entirely the surface resist-

ance on the flame side, hence when the resistance of the metal of the tubes is relatively so small, it does not change the final result at all. I think that probably was the case in Mr. FitzGerald's experiments. In a steam boiler the flow of heat from the flames to the water would probably not be appreciably less if the tubes were made twice as thick, just as Mr. FitzGerald found in his experiments.

MR. FITZGERALD: That is probably the case in these experiments, and shows that various laws must be considered. It is difficult to take the laws of conduction, radiation, etc., separately and then combine them and make calculations; at least, this is dangerous in actual practice. My communicated discussion bears on the necessity, at the present time, of making experiments so as to get trustworthy results quickly.

DR. C. B. THWING: I wish to refer to the point mentioned by Mr. Hering in regard to measuring the temperature of the surfaces exposed to radiation. I was interested in Mr. Hering's suggestion with regard to the use of wax for securing an indication of the temperature of the surfaces of a boiler. If you cover a rough surface with wax it will not radiate the same, and therefore will not have the same temperature as the other portions not covered with wax. The correct way is to measure the radiation by the pyrometer, the same as is used in measuring high temperatures. The surface radiating energy is large, and it can be used in that way. The radiation pyrometer does not touch the surface and does not change the surface, and that is the only way you can accurately measure temperatures of dark radiating surfaces.

DR. HERING: I, of course, meant using little fragments of wax, not covering the whole surface. I question the accuracy of a radiation pyrometer at such low temperatures.

PRESIDENT WHITNEY: Wax has a very indifferent melting point; it is difficult to get a material like that which will melt at a definite point.

DR. HERING: Such materials with definite melting points could, I think, be made. We do not now seek for scientific accuracy; for the practical purposes of the engineer it seems to be amply

satisfactory, and is much less expensive than the radiation pyrometer.

PRESIDENT WHITNEY: It is true that a lot of our published work must come from those who do not use pyrometers.

DR. RICHARDS: I think it would be more practicable to use some of the more easily fusible alloys, in little sticks or wires; these could be inserted in small holes in the side of the furnace. They can be graded, with different but definite melting points, so as to cover the entire range of temperatures likely to occur. There are alloys melting as low as 80° C.

MR. L. H. DUSCHAK: I would like to ask Dr. Hering if he can give me some idea of the approximate error in making a measurement of the surface temperature with a very fine thermocouple, which will come to temperature in a few seconds? Would the error be large enough to throw out the results entirely?

DR. HERING: That depends largely on the resistivity of the material forming the surface. I know in certain experiments made with a strip of metal, which was heated electrically, to determine the radiation of the heat from the surface, the thermocouple was touched to the strip in order to determine its temperature, and it was found that the strip immediately became black where it was touched, although it had been red hot before, thus showing that the real temperature was decidedly higher than that which the couple recorded. The error was so great that the results were absolutely worthless. It seems to me that on a surface of refractory material the error would be very much greater, because the flow of heat to that cooled spot would be still slower.

DR. THWING: If it is desired to measure the temperature of an outer wall by means of a thermocouple, it would be advisable to make the thermocouple as small as possible and to insert it at some little distance from the point where the temperature is to be measured and to a depth of several inches into the wall, bending it back so that it would emerge flush with the surface at the point to be measured. The body of the thermocouple would then have the same temperature as the wall, and would not tend to reduce the temperature at the surface, as would be the case where a cold thermocouple is held against the surface.

DR. HERING: This complicates matters greatly; it might do in the laboratory, but in practice one often wants to measure the actual surface temperature at numerous points, and one does not always have an innumerable number of couples at one's disposal. Moreover, the outside of a furnace is often sheet iron. I question, however, whether the results even in the laboratory would be reliable, as the additional mass of the bent part would probably change the thermal conditions in the whole region. At best it would be uncertain, hence unreliable.

MR. W. C. ARSEM: I understand it has been shown, for a number of poorly conducting substances, that the electrical resistance is a logarithmic function of the temperature. We may find later that the thermal resistance obeys the same law. This law for the electrical resistance holds for substances as widely different as porcelain and linseed oil. The application of the Nernst equation $\frac{dK}{dT} = -\frac{Q}{2RT}$ to the relation between conductivity and temperature for poorly conducting bodies has been studied by Rasch and Hinrichsen, Zeitschr. Elektrochemie, **14,** 41, 46 (1908), and by Königsberger, Phys. Zeitschr., **8,** 833 (1907).

DR. RICHARDS: I have used Mr. Thwing's method of radiation, and found it very satisfactory in laboratory experiments in measuring the temperature of surfaces with a very delicate radiation pyrometer, down to about 100° C.

MR. F. W. ROBINSON: If we are looking for methods of testing our theoretical hypotheses we cannot afford to take into consideration the cheapness and convenience of the methods of measurement. We must be guided as far as practicable by the one object, accuracy. Now, although graded waxes and easily fusible metals are cheap and simple to operate, they scarcely meet our requirements as regards reliability and accuracy, and it seems to me that the most suitable instrument for these measurements we at present possess is the total radiation pyrometer.

DR. HERING: It is, of course, desirable to get data accurately, but at present we have nothing which can even approach accuracy, and we are very thankful for even approximate data.

PRESIDENT WHITNEY: We do not know today whether the conductivity of insulating materials obeys any simple laws or not.

MR. S. S. SADTLER: Mr. Thwing suggests that low temperatures can be measured by the total radiation pyrometer. It seems to me that 100° C. is not very low for the outer walls of well-insulated furnaces.

DR. THWING: There is no trouble in measuring the low temperatures. It is a question of the size of the surface. If you have a larger surface, you can collect the energy from a larger surface. The rate of change of energy is not so great as higher up. The advantageous place for measuring by total radiation is the high temperature, since the radiation is more active at that point, but with a large surface you can measure lower than 100° C.

DR. W. C. BRAY: The thermocouple should be actually in position all the time. Any contact method, thermometer, wax or alloy, *i. e.*, anything applied from the outside, is almost certain to give inaccurate results. If a suitable form of thermocouple is used, and it is placed inside the surface, so as to disturb as little as possible the arrangement of the material, there does not seem to be any reason why accurate results should not be obtained even at low temperatures.

PRESIDENT WHITNEY: Another thing occurs to me, and that is the use of the resistance of a metal which is imbedded in the walls in any suitable way. You can then determine the temperature of the wall through the resistance of the wires imbedded in it.

DR. HERING (*Communicated*): Replying to the last remark of President Whitney, a resistance thermometer would probably give good results, as it abstracts very little heat; but as it must be imbedded, there must either be a hole there or it must be filled with some material, and in either case there is a change in the very place where one wants to measure the temperature. Moreover, such a resistance thermometer could not be imbedded in the outside steel shell of a furnace, and that is the very part we generally want to know the temperature of, as it may be very different from that of the material behind it. The wire

coil might, however, be pressed against such a steel surface with a wad of cotton.

After hearing the above discussion I still think that sufficiently good results for practical work could be gotten with fragments of graded waxes stuck on the outside surface at various places. It has the advantages of simplicity, cheapness and durability. It is not a case where great accuracy is necessary. One should not be deceived into believing that one is making an accurate measurement simply because the instrument itself is accurate; it is quite as important that the application of the instrument should not alter the condition of the thing to be measured.

Replying further to Mr. FitzGerald's discussion, it seems to me that there are so many modifying circumstances and sources of error in his experiments that it would be quite dangerous to conclude from them that thicker walls are very little better than thin ones. If this really is the case, then less questionable proofs than those he gives are required. It would be very unwise to claim that because no body ever falls with the velocity which it should have theoretically, that we should therefore discard the very useful fundamental laws of falling bodies. If facts do not agree with fundamental laws, we should first try to find out whether there is not some good reason for the difference before we overthrow the fundamental laws. In many cases entirely wrong and very misleading conclusions have been drawn from experimental results because the fundamental laws were either not known or were not duly considered.

In his experiments the inside was heated by radiation and hot air, not by liquid contact, as in most furnaces; hence the inside surface resistance was probably quite great. Moreover, he did not consider the flare. It may also be questioned whether his temperature measurements were really reliable. If the flow of heat was very small the inaccuracies would naturally be very great. Moisture in the bricks is another very serious source of error until they are thoroly dried out.

I would consider it very dangerous to draw hasty conclusions from such experimental results as these.

If, however, it should be definitely established that the heat insulation resistance of a furnace is chiefly a surface resistance and only to a slight extent due to the thickness of the walls, it

would be very important to know it, as it would make a considerable difference in the design of furnaces. I called attention to this possibility in other papers. The only thing we really know definitely now is that we know very little about the whole subject.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

EXPERIMENTS ON HEAT INSULATION.

By F. A. J. FitzGerald.

At the Twentieth General Meeting of this Society a paper[1] was presented describing an electric furnace experiment in which it was found that the heat losses were so great that the furnace was not commercially practicable. It was also observed that by placing a layer of special heat insulating bricks wherever practicable on the outer walls of the furnace the heat losses were much diminished.

The very serious consequences of not attending properly to heat insulation led to an attempt to study the subject of heat losses, and the following paper describes some of the preliminary experiments.

Energy which should be usefully employed in the electric furnace is lost in various ways: Current leakage, generation of heat in the cables and other means for conducting the current into the furnace, conduction, convection and radiation of heat by the furnace walls, etc. In many furnaces there can be little doubt that the most serious loss of energy is that due to the escape of heat through the walls.

In the study of this subject we have no data which enables us to make calculations of the heat losses which will occur with different materials and under various conditions. No doubt there have been careful and valuable investigations made on the heat conductivity of materials and some experiments on the emissivity of hot bodies. Little information is available as regards convection. When such data as we have on these various causes of heat loss are examined and an attempt made to calculate probable losses the results are usually most unsatisfactory. On the other hand it is still more unsatisfactory to construct

[1] "Note on an Unsuccessful Furnace Experiment," F. A. J. FitzGerald. These Transactions **20**, 89 (1911).

electric furnaces and find that they are commercially impracticable because the heat loss through the walls is such a large percentage of the total heat generated in the furnace.

The ideal method of studying the subject would be to make the necessary experiments to determine the heat conductivity of the

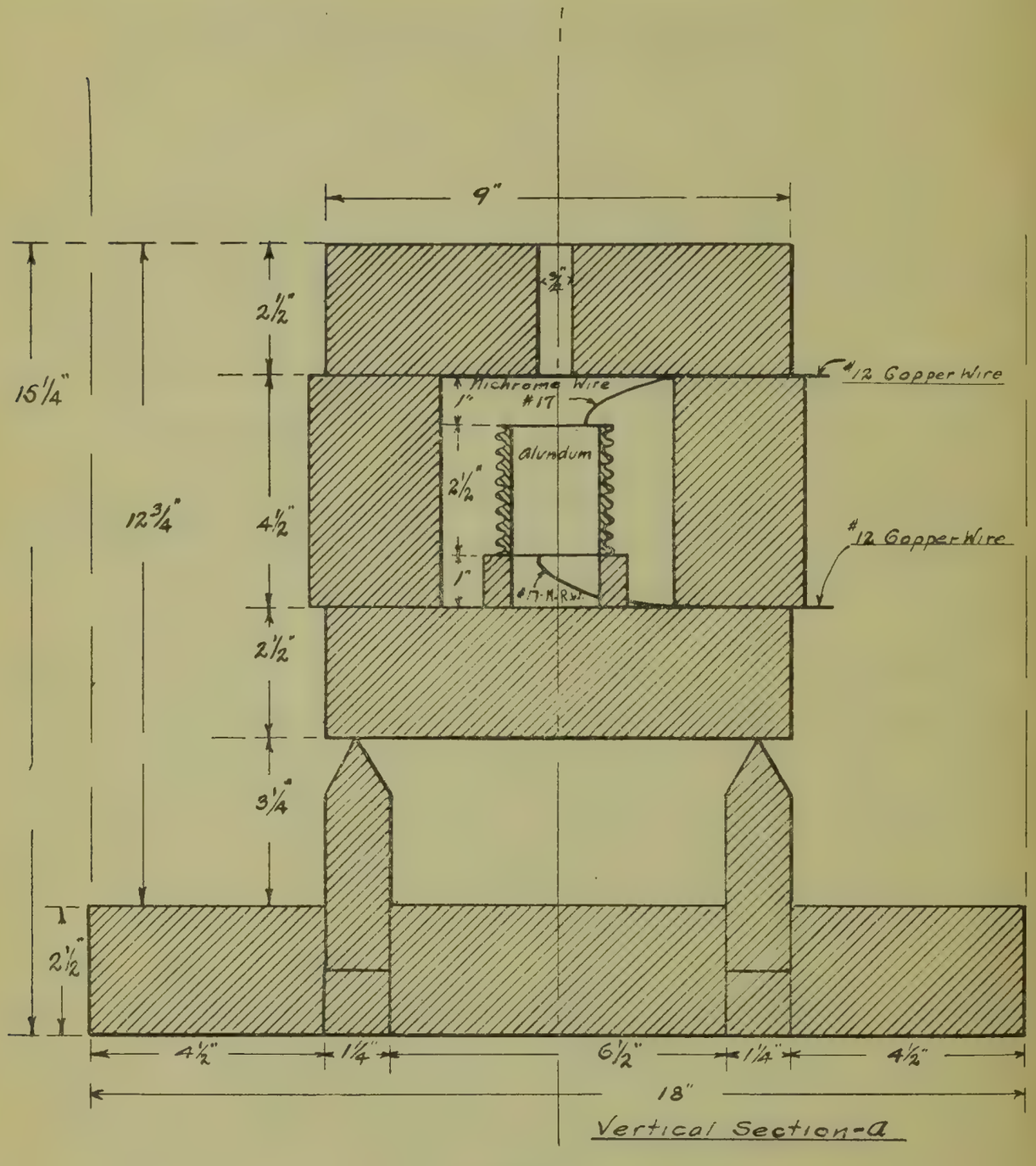


FIG. 1.

various materials to be used in constructing the walls of furnaces, to make measurements of the emissivity of the heated walls and so forth. But when the plans for such an investigation are made it is soon seen that much time and expense is involved. Under these circumstances it was thought to be more immediately

useful to determine by comparatively simple experiments what materials would give the minimum loss of heat. By such work a great many materials could be immediately rejected and those which gave good results would be more fully investigated.

The apparatus used in the experiments is shown in Figs 1 and 2. The furnace is constructed of the bricks under investigation and is heated by means of a resistor of "Nichrome" wire through which the current is passed. The resistor is connected to the source of current through a rheostat so that the rate of generation of energy in the resistor can be regulated, and means are provided for accurately measuring this rate. The method of

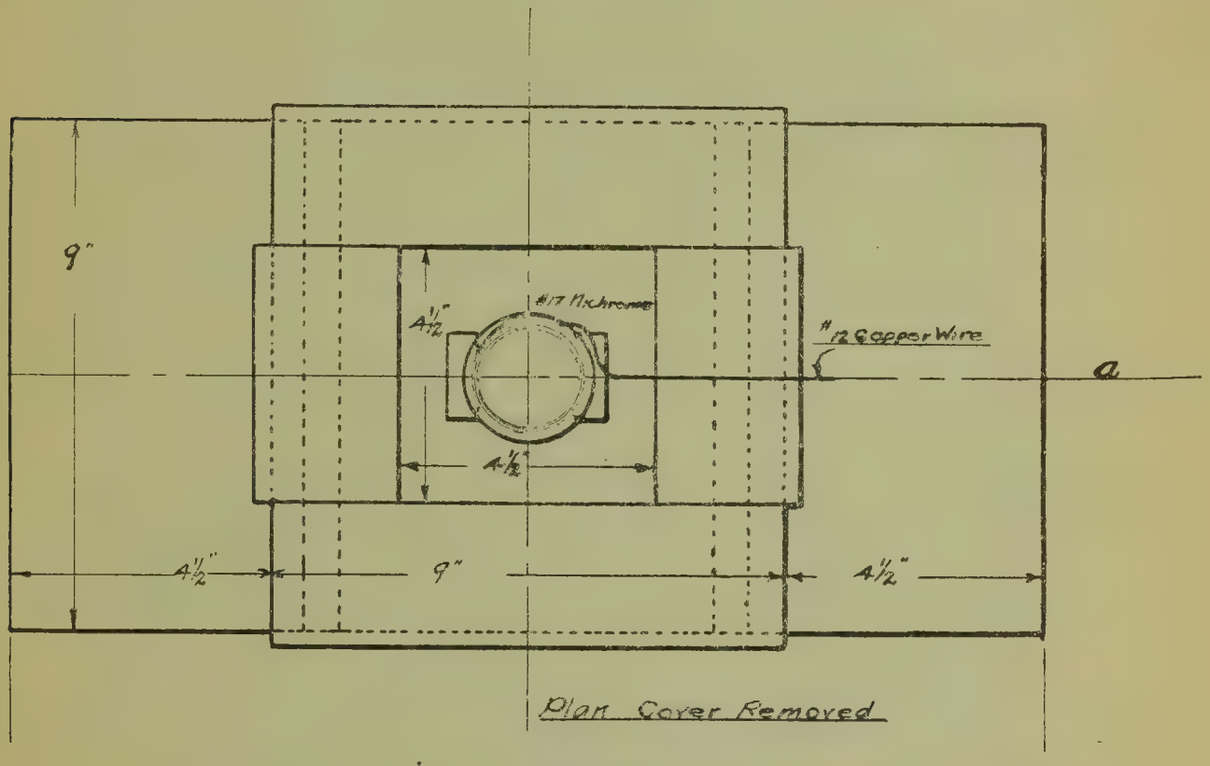


FIG. 2.

making a test is to regulate the current so that a definite temperature is reached in the furnace and then to continue heating until the temperature becomes perfectly constant. As a rule a single determination takes several hours and the temperature is not considered constant until the readings of the pyrometer show no variation for at least two hours. When the temperature is constant the rate of generation of energy in the resistor is determined and this gives the rate at which heat is escaping through the furnace walls, neglecting what escapes by conduction through the leads going to the resistor and through the wires of the pyrometer thermo-couple. In nearly all cases four

determinations at temperatures ranging from 200° to 900° were made for each of the materials tested.

From the data obtained as described above, curves were plotted in which the abscissas are temperatures and the ordinates watts.

In Fig. 3 are shown the curves obtained with several different bricks.

No. 2 is a fire brick of moderately good quality, that is to say, it is not of any special make. It was the brick used in con-

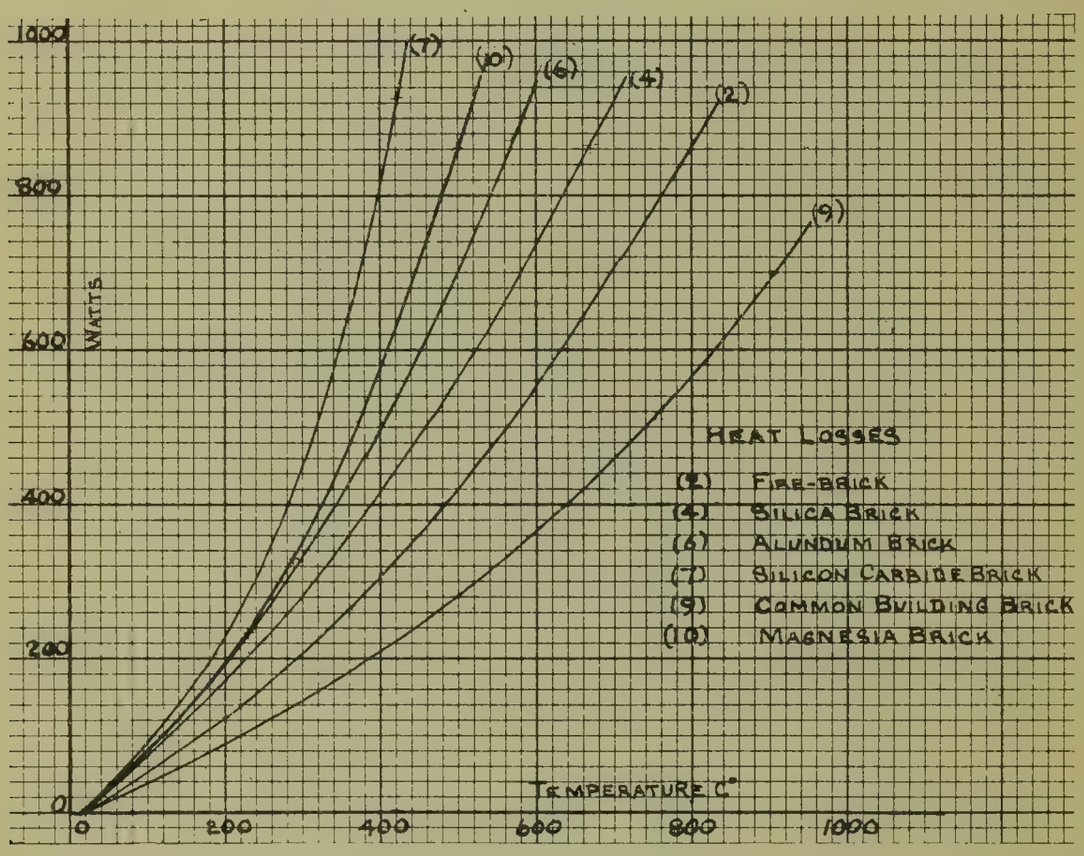


FIG. 3.

structing the furnace referred to in the paper mentioned above.[2] The maximum temperature reached in the brick testing furnace was 800.°

No. 4 is the curve for a silica brick. It is interesting to note that in the paper already referred to it was said:

"It was recognized that silica brick are better heat insulators than fire brick, as may be seen from Wologdine's determinations[3]

[2] *Ibid.*

[3] Electrochemical & Metallurgical Industry, Vol. VI (1909), page 383.

which show that the heat conductivity of silica is 0.0020 and of fire brick 0.0042."[4]

It appears, however, that in spite of its low heat conductivity this particular silica brick is not a satisfactory insulator. The maximum temperature reached with the silica brick was 670.° The heat loss here was 36 per cent. greater than with the fire brick. It is not very safe to theorize as to the cause of this phenomenon, but it looks as though the radiation from the sur-

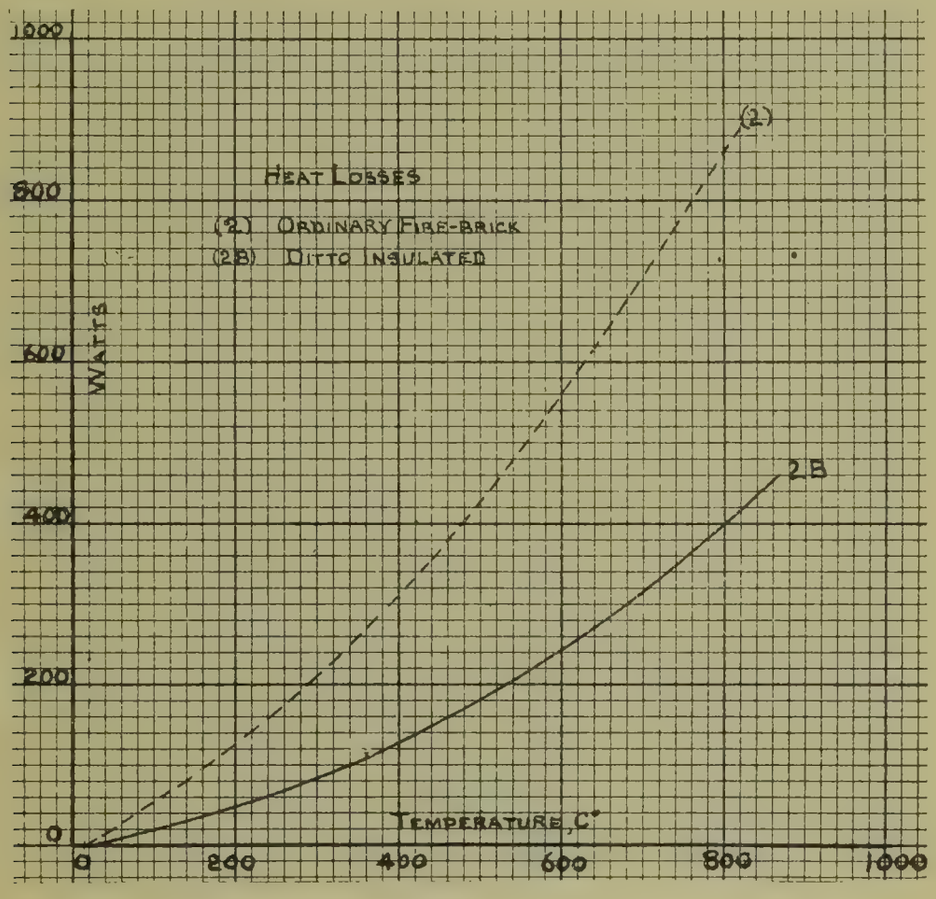


FIG. 4.

face of the silica brick is very much greater than from the ordinary fire brick. The vast differences due to the nature of the radiating surface is not so surprising if a familiar household phenomenon is considered, viz., the great difference in the rate of cooling of the common black iron kettle and the polished silver tea pot.

No. 6 was obtained from an alundum brick, one of the highly refractory ones made by the Norton Company. The transmission

[4] These Transactions, Vol. 20, 89 (1911).

of heat was so rapid with this brick that the maximum temperature obtained in the furnace was only 570°. This illustrates well the value of such alundum refractories as crucibles, muffles, etc., where it is desirable to have as efficient transmission of heat as possible.

No. 7 is the curve for a brick made of silicon carbide. The brick is pure silicon carbide, that is, no bond is used in making it. The transmission of heat is extremely good with this brick

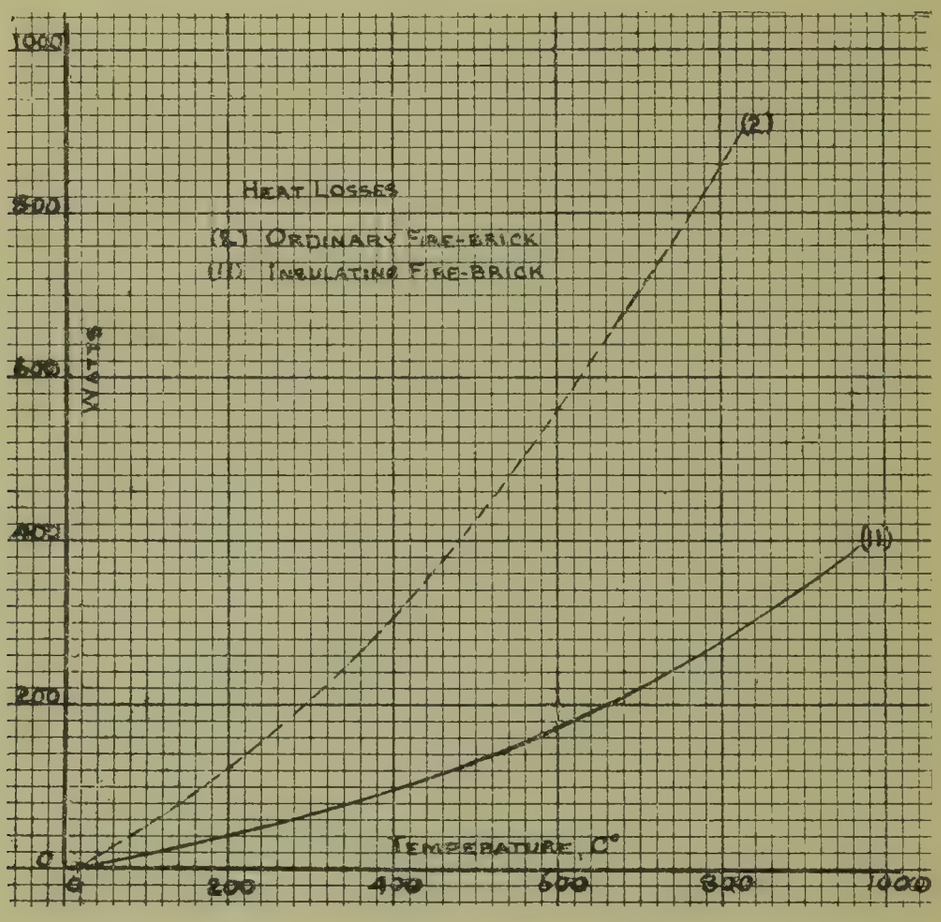


FIG. 5.

so that the maximum temperature reached in the furnace was only 420°. Comparing this brick with the fire brick (2) when the temperature in the furnace was the same (420°) it is seen that the rate of escape of energy is 920 watts and 300 watts respectively, or more than three times as great in the case of the silicon carbide brick.

Curve No. 9 is that for an ordinary red building brick of the cheapest kind. It is seen to be the best insulator of any of this lot, the heat losses being as much as 34 per cent. less than those for the fire brick (2) at a furnace temperature of 800°.

Curve No. 10 shows the results obtained with a magnesia brick. This was of a standard kind made of brown magnesia and not the Grecian magnesia variety.

In Fig. 4 are shown the results obtained, first with the ordinary fire brick (2) and then after covering the whole furnace built of this brick with a 25 mm. (1 inch) thickness of a special heat insulating material kindly supplied by a well known manufacturer. It will be observed that this material reduced the heat losses by more than 50 per cent.

In Fig. 5 is a comparison of the heat losses obtained with the ordinary fire brick (2) and a brick specially constructed for heat insulation. Here it will be observed that in the case of the special insulating brick the heat losses are reduced 68 per cent.

The first object of this work is to make a study in the quickest way possible of the heat insulating properties of various kinds of brick used in building furnaces and get some notion of the amount of heat lost with such materials. The ultimate object in view is the production of a heat insulating article, the cost of which will be less than that of the watt-hours uselessly dissipated through furnace walls.

The foregoing paper represents some of the results obtained in the preliminary investigation of the subject. There have been many data obtained on other bricks made with the object of efficient insulation, and it is hoped that these will be ready for presentation at the autumn meeting of this Society.

FitzGerald and Bennie Laboratories,
Niagara Falls, New York.

DISCUSSION.

DR. CARL HERING: I agree entirely with Mr. FitzGerald in the statement that good empirical data is lacking, as I have said before in published articles. But it seems to me that it is also necessary to study the various fundamental laws, that is, to make analytical researches, in order to be able to interpret the empirical

results correctly. Unless we do this we will get a jumble of empirical data that does not mean anything and that will not help us. In my opinion the analytical study should go hand in hand with the determination of empirical data.

MR. F. A. J. FITZGERALD: I agree with all Dr. Hering says.

DR. R. AMBERG: I ask whether any of these insulating materials can be used in eddy currents.

MR. FITZGERALD: Some of these are not insulating materials; for example, the alundum and silicon carbide brick are not. The best heat insulating material is shown in Fig. 5, curve 11. It is a brick made of Kieselguhr; but it would not be acceptable as a lining material. If you have a good lining material and then put Kieselguhr brick outside, very satisfactory results can be obtained. The Kieselguhr brick itself is able to stand a temperature of 1100° C.

PRESIDENT WHITNEY: Were any experiments made to see if you could modify the surface of these bricks?

MR. FITZGERALD: We made some specially surfaced bricks. We built the furnace with the ordinary fire-brick, and first painted the bricks with lampblack, and then with aluminum. In the case of the bricks painted with the aluminum the insulation is more satisfactory. We also tried painting them with white lead, but the heat losses were somewhat increased. Convection is very important also; that point is brought out very strongly in Wologdine's papers.

PRESIDENT WHITNEY: I am very much interested in the subject of painting the surfaces of the bricks. Can you give us any further data?

MR. FITZGERALD: I have made some investigations and have some curves bearing on the results, but not here. I will try to publish them at sometime, because I think that this is important. The experiments show that the nature of the surface has quite a serious bearing on the conductivity.

DR. HERING: This effect of the surface resistance is shown by the well-known fact that a highly polished coffee pot will keep

the coffee hotter than one which is not polished. When the outside surface of a heat conductor is highly polished this surface becomes a much better heat insulator.

Mr. M. M. Kohn: Is the heat insulation more the result of cellular spacing, or is it more or less real non-conductivity of the solid material? I ask this question for this reason: As far as my own experiments have gone the material is not of the greatest importance, but rather the shape in which it is used. The material itself, magnesium oxide for instance, in the form of powder, while being a relatively poor conductor of heat in its normal condition, loses this property very rapidly when used in a furnace in the ordinary way. The reason for this, as far as I have been able to demonstrate it, is its peculiar property of packing or solidifying in the furnace. When this occurs, its heat conductivity is enormously increased, and consequently the efficiency of the furnace drops rapidly because of the increased radiation. In some of the experiments which I have made along this line I have dispensed entirely with substances which have a tendency to pack, and, in fact, do not use anything of the nature of powder for this purpose; that is to say, I do not use it in its natural form, but preferably as a mixture of various silicates, magnesium oxide and calcined magnesia, etc., long asbestos fiber, which is then mixed with silicate of soda so as to make a very thick, dough-like mixture. This is then allowed to dry, after which it is baked at a temperature just below red-heat, and is then crushed and broken up into small pellets. This gives an ideal form of heat insulation, firstly, because the pellets are very porous themselves, and, secondly, because no matter how tightly they may pack, they form a cellular or air space heat insulator surrounding the inner chamber, and I believe it is a conceded fact that air at rest is about as good a non-conductor as any of the artificial substances we use.

I have not yet completed my experiments on this subject, but from what has already been done, am satisfied that the perfect heat insulation will be along these lines.

Mr. L. H. Duschak: The effect of air cells in heat insulating material will vary with the temperature at which the materials are used. At high temperatures heat is transferred to a large

extent by radiation, so that large air cells are a disadvantage. At low temperatures the air cells are much more effective.

Mr. FitzGerald: The experiments I have made lead me to believe that the porosity has a great deal to do with it, although a good deal depends on the nature of the material itself. I have used insulating material in spaces between furnace walls, and found by experience that when it was packed down it did not insulate the walls as well as when it was loose.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society, in Boston, Mass., April 18, 1912, President W. R. Whitney in the Chair.

THE THERMAL RESISTIVITY OF INSULATING MATERIALS.[1]

By C. P. Randolph.

Most of the measurements of the thermal resistivity of insulating materials that are to be found in scientific literature were made under such conditions that the temperature of the surface from which the heat flows to the surroundings could not be measured directly, or else they were made so many years ago that the instrumental facilities, such as electrical heating, etc., were very limited. The apparatus here described was designed with a view to making a large number of measurements on compressible materials, under varying conditions of density, temperature, thickness, direction of flow of heat, etc. With this class of substances (such as lampblack, magnesia-asbestos, etc.) the contact resistance is eliminated. The material is pressed between two plates, so that the space between the plates and the particles of insulation cannot be greater than that between any two particles in the interior of the material. The effect of side losses is eliminated, and at the same time no formula for a special geometrical shape has to be used. It requires about two hours to bring the material to constant temperature and to take the readings necessary for calculating the resistivity.

The apparatus consists essentially of two copper plates, one heated by electricity to the desired temperature, the other cooled by water. Between these is placed the material whose thermal resistance is to be measured.

The accompanying figures show clearly the construction. *A*, Fig. 2, is the "hot plate," made of copper ¼ inch (0.6 cm.) thick. It is supported by the three bolts shown, so that the material being measured can be compressed with a good deal of force when desired. The resistance unit, made of calorite ribbon so wound on mica discs as to give good heat distribution, is

[1] A communication from the Research Laboratory of the General Electric Company.

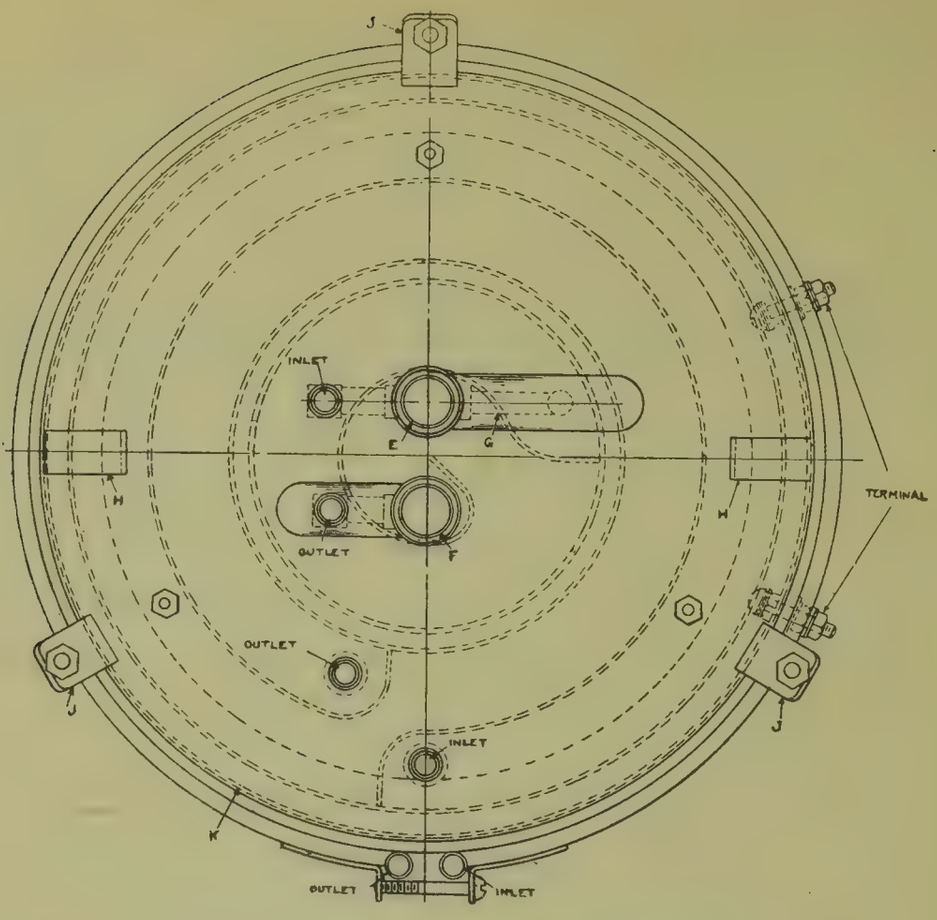


FIG. 1. Plan.

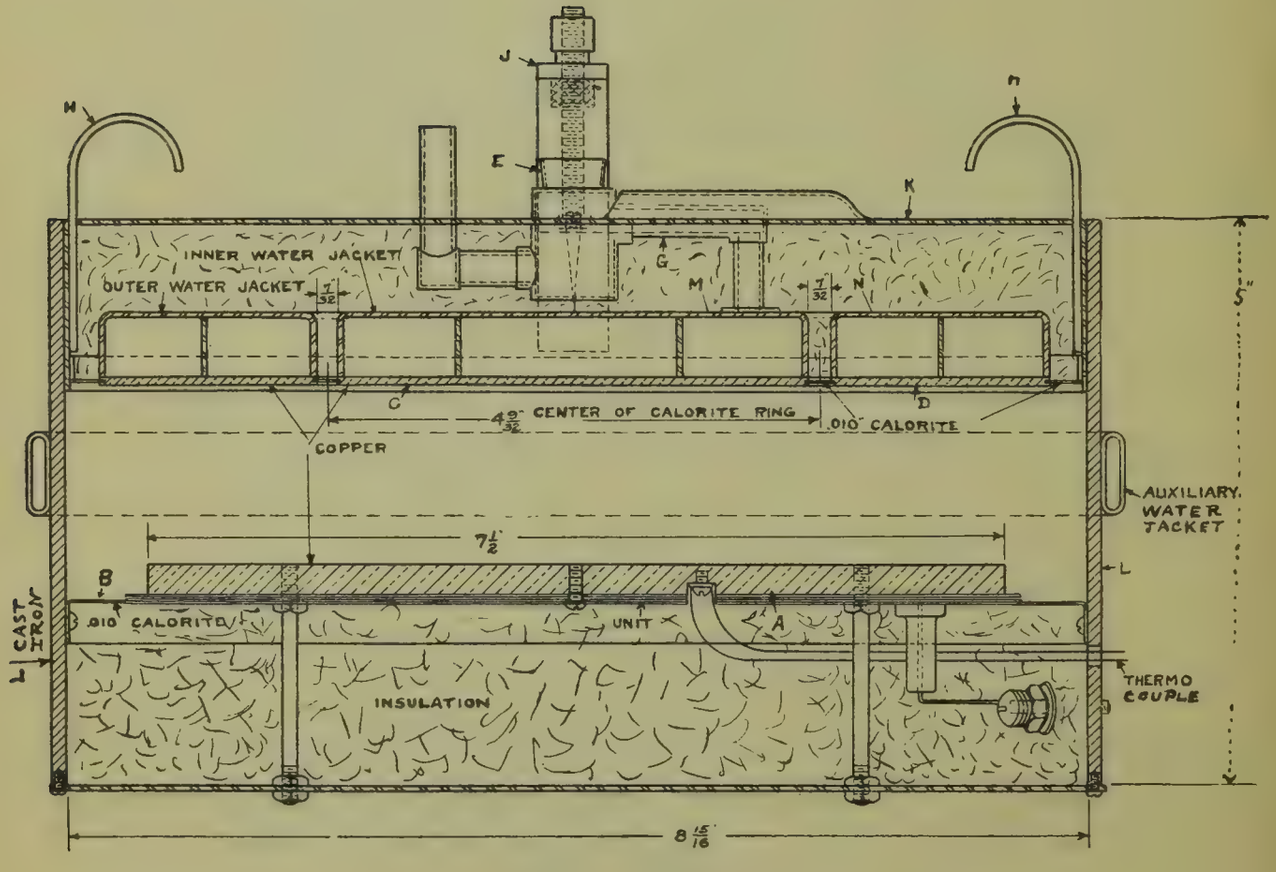


FIG. 2. Section.

clamped between two mica discs to the hot plate by the calorite sheet *B*. The plate *A*, being of thick copper, is maintained at a very uniform temperature. The sheet *B* is made of calorite 0.01 inch (0.25 mm.) thick, so that the loss of heat to the sides is reduced to a minimum, calorite having a very high thermal resistivity. A platinum-platinum-rhodium thermo-couple is clamped to the lower side of the copper plate *A* with a screw,

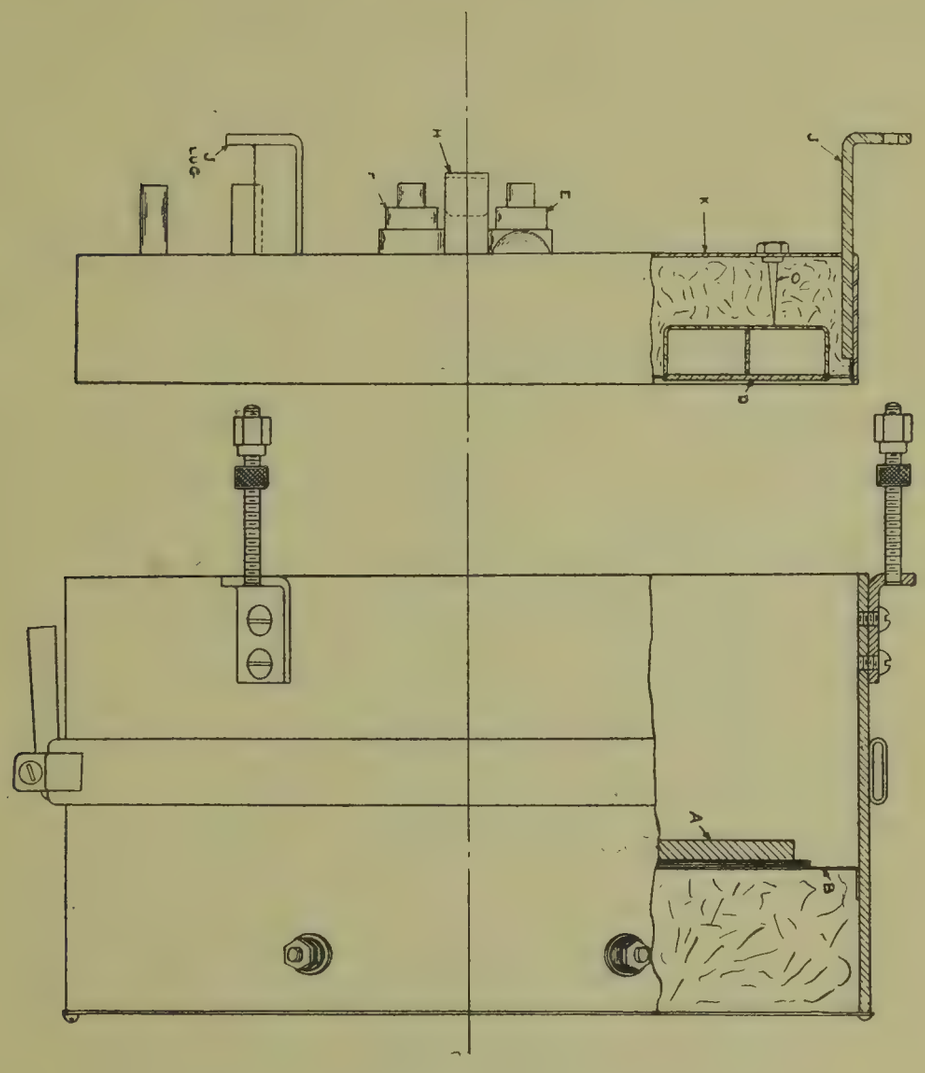


Fig. 3. Elevation, Cover Removed.

and is brought out through a hole in the cast-iron cylinder *L* to the cold junction. The space below the plate *A* is permanently filled with insulation, so that the plate can be quickly brought to any temperature. Above *A* is placed the material whose resistance is to be measured, in any desired thickness from 2½ to ½ inches (6.3 to 1.3 cm.), the entire cover *K* being easily removable for changing materials, as shown in Fig. 3.

This cover *K*, Fig. 2, contains two of the water-jackets. *C* is

a copper disc, and *D* a flat copper ring, each $\frac{1}{16}$ inch (0.16 cm.) thick, to which are soldered the spinnings *M* and *N*. These water-jackets are so partitioned that the water is forced to circulate spirally through them, as shown by the dotted lines in Fig. 1. The water flows into each of them at the same temperature, and the rate of flow is so regulated that the temperatures of the outflowing water never differ more than 0.1° C. A calorite ring connects *C* and *D*, and another calorite ring connects the ring *D* with the wall *K* of the cover. Thus we are sure of very little interchange of heat between *C* and *D*, or between *D* and the walls. The space above and between these water-jackets is filled with insulation, so that there may be as little interchange of heat with the walls and with each other as possible. The pointed rods *O*, Fig. 3, support the water-jackets so that the cover can be pressed down tightly. Of course, there are losses from the edges of the material whose resistance is being measured, in the space above *A* to the walls, thus distorting the lines of flow of heat at the edge. But the outer water-jacket forms a "guard ring" for the inner one, so that the isothermal lines, perpendicular to the direction of the flow of heat, are practically horizontal over the area covered by the inner water-jacket. Only this area is considered in the calculation of the resistivity. It is assumed that the heat flowing to the calorite ring connecting *C* and *D*, Fig. 2, divides evenly, and therefore the effectual area is that enclosed by the center line of the small calorite ring.

In order to still further prevent interchange of heat between the walls and the cooling water, an "auxiliary" water-jacket is soldered to the outside of the cast-iron wall. The handles *HH*, Fig. 2, are provided for removing the cover. The three lugs *JJJ*, Fig. 1, are for adjusting the cover for the desired thickness and density of the insulating material being measured.

Fig. 1 shows the arrangement for the inflowing and outflowing water. Rubber tubes are attached at the points marked "Inlet" and "Outlet," the water supply for all three jackets coming from the same main and therefore at the same temperature. The flow of heat through the material is determined by the rise in temperature and the rate at which the water flows through the inner

water-jacket. A constant rate of flow is secured by allowing the water from the supply mains to flow into a tank fastened to the ceiling of the laboratory and automatically kept filled by a float-valve. The temperatures of the inflowing and outflowing water are measured in the cups *E* and *F*, respectively. This rise in temperature is measured directly with a sensitive thermo-couple made up of six lengths of "Advance" wire and seven lengths of calorite wire, brazed end to end; *i. e.*, the couple consists of alternating lengths of calorite wire and "Advance" wire brazed together. One set of junctions, the "cold junction," is in the water flowing through cup *E*, and the other set, the "hot junction,'" is in the cup *F*. Thus the rise in temperature is directly proportional to the difference of potential of the two sets of junctions. All electromotive-force measurements were made with a Leeds & Northrup potentiometer, read accurately to thousandths of a millivolt. One degree Centigrade equals about four millivolts, with the above arrangement, and therefore the rise in temperature of the water need never be more than 0.4° for 1 percent accuracy. This thermo-couple we have found very satisfactory. It is held in place in the cups *E* and *F* with rubber stoppers. In order to make sure that the actual temperature of the inflowing water is measured, the cup *E* is connected to the wall of the water-jacket by the long tube *G*, which has very thin walls, thus making the interchange of heat between the cooling-jacket and the air very small.

A standard compression for powdered and fibrous materials of low density was adopted, *viz.:* the material was packed as much as possible by tapping, the thickness measured, and the material then compressed 25 percent of the thickness it assumed when tapped. Unless otherwise specified, this is the condition which determines the densities given below. All densities were measured by weighing the total amount of the material used for the measurement.

The measurements were easily made with an error no greater than 2 percent. But, of course, some of the materials are not of uniform density throughout, and the resistance varies as much as 5 percent with different samples of the same material.

T = temperature of the side at which the heat enters the insulation.

t = temperature of the side at which the heat leaves the insulation.

A = effective area of cross-section in square inches.

L = length (thickness) of insulation in inches.

W = watts.

D = density in grams per cubic centimeter.

$R' = \frac{T-tA}{WL}$ = resistivity, expressed in "thermal ohms" per inch cube[2] = degrees per watt per 1 inch cube.

R = resistivity, expressed in thermal ohms per centimeter cube = 2.54 R'.

R'' = resistivity, expressed in degrees per calorie per second per centimeter cube = 10.6 R'.

In the table, t is not given, but was 4° to 10° in every case. T is given to the nearest hundred, from which it did not differ over 10°.

No. Material.	D	T	R	R'	R''
1005—85% magnesia-asbestos. This sample was not dried. The measurements were made in the order given. Heating to 600° C. has evidently permanently injured the insulation.	0.216	100	1500	590	6250
	"	200	1530	603	6400
	"	300	1530	601	6380
	"	300	1540	605	6410
	"	400	1450	572	6060
	"	500	1450	570	6050
	"	600	1220	482	5110
	"	500	1320	518	5500
	"	400	1360	537	5700
1008—"Air-cell" asbestos. Chars at 300° C.	0.250	100	1110	437	4640
	"	200	1020	403	4270
	"	300	915	360	3820
1009—"White asbestos fibre," from Eimer & Amend.	0.279	500	1240	488	5180
1006—"White asbestos fibre, acid washed," from Eimer & Amend.	0.201	500	1280	503	5340
1010—"Asbestos wool," from Eimer & Amend. Dried at 350° C.	0.200	500	1120	440	4670
1013—"Long fibre asbestos," from Eimer & Amend. Dried at 350° C.	0.293	500	1410	556	5900

[2] Hering, Met. Chem. Eng., 9, 13 (1911).

No. Material.	D	T	R	R'	R''
1012—Mineral wool from Eimer & Amend. Dried at 350° C.	0.427	500	1460	573	6080
1014—Steel wool, No. 2, made by the American Steel Wool Mfg. Co. It is seen that increasing the density 100% increases the resistance only 12%. This material is a good illustration of the fact that it is not the composition that determines the resistance of these materials, but the state of division. The resistivity in this form —as steel wool—is about 700 times that of a steel bar.	0.076	100	1120	443	4700
	0.101	100	1160	457	4850
	0.152	100	1260	498	5280
1002-1—"Diatomaceous earth and asbestos." This sample was not dried.	0.330	100	965	380	4030
	"	200	1200	473	5010
	"	300	1330	525	5570
	"	400	1500	592	6280
	"	500	1160	455	4820
1002-2—"Diatomaceous earth and asbestos." Dried three days at 300° C.	0.330	400	1470	577	6120
	"	300	1370	538	5710
	"	200	1390	548	5810
106-A—"Poplox." Resembles popcorn. Made from Na_2SiO_3, by popping.	0.023	200	2470	973	10300
	"	300	1810	713	7560
108-A—"Poplox." Dried at 500° C. Resembles popcorn. Made from Na_2SiO_3, by popping.	0.093	200	2640	1040	11000
	"	300	2440	958	10200
	"	400	2000	786	8340
	"	500	1500	590	6250
1015-1—"Asbestos fire-felt." This is a very light, but self-sustaining material.	0.116	200	2240	882	9350
	"	300	1510	597	6330
	"	400	1280	503	5330

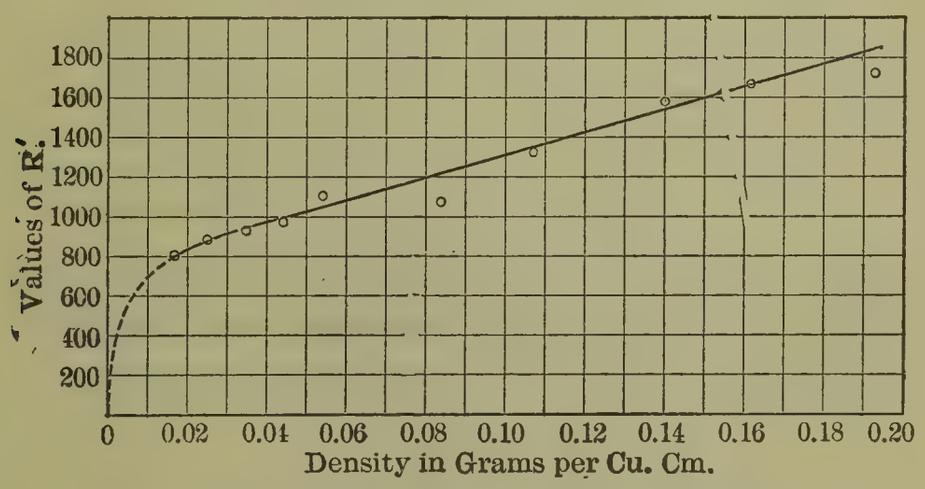


Fig. 4. Curve showing relation between the density and thermal resistance of pure wool wadding.

No.	Material.	D	T	R	R'	R''
1016	"Asbestos sponge-felt." Made up of layers about 1/64 inch thick, that resemble asbestos paper. Dried at 150° C. before measurement.	0.551	100	2590	1020	10800
		"	200	2240	883	9360
1017	Pure clean woolen fibres. Dried at 100° C. The curve, Fig. 4, shows the regularity with which the resistance varies with the density. Of course the density throughout a sample will never be uniform, so that we cannot expect exact proportionality.	0.0153	80	2040	802	8500
		0.0153	100	2040	802	8500
		0.0250	100	2260	888	9410
		0.0352	100	2370	932	9890
		0.0444	100	2460	968	10300
		0.0545	100	2790	1100	11700
		0.0823	100	2720	1060	11300
		0.106	100	3380	1330	14100
		0.140	100	3990	1565	16700
		0.163	100	4250	1670	17700
		0.192	100	4400	1730	18400
1018	"Fire roll." This is a heavy cloth about ¼ inch thick, and is made of pure long-fibre asbestos. Dried at 500° C. for twelve hours before testing.	0.575	100	1240	487	5160
		"	300	1260	497	5270
		"	500	1240	489	5180
1007	Cotton.	0.021	80	2160	852	9040
		"	100	2180	858	9100
		0.101	100	3360	1320	14000
1019	Eiderdown. Dried at 150° C	0.00214	100	2170	853	9050
		"	150	1580	623	6600
		0.0788	150	4130	1620	17300
		0.109	150	5160	2030	21500
1020	Finely ground quartz. Through 200 mesh. Dried at 500° C.	1.05	500	984	387	4100
1021	"Granular" quartz. Particles irregular, but about $\frac{1}{16}$ inch diameter.	1.64	500	389	153	1620
1022	Coarse quartz. Particles about ⅛ inch in diameter.	1.55	500	338	133	1410
1023	Cabot's No. 5 lampblack.	0.193	100	3230	1260	13500
		"	300	2640	1030	11000
		"	500	2230	878	9310

Further measurements of the thermal resistivities of materials of various kinds, such as bricks, porcelain, etc., will be made.

I am indebted to Mr. M. J. Overholser for most of the experimental work.

DISCUSSION.

DR. CARL HERING: I take pleasure in complimenting the author on his very excellent paper. The results are very valuable, since they at last give us some data which appears to be very much better than that which we have had to collect from various sources of perhaps questionable reliability.

One of the especially interesting features is that the author finds the resistances becoming greater as the pulverized materials are compressed more and more. We had formerly been taught that the looser such materials the better the insulation. Mr. Randolph now shows us that this was one of our inherited fallacies.

I cannot quite agree with him that the contact resistance is eliminated entirely in his method. If there is a metal plate next to the insulating material it would, I should suppose, abstract the heat very quickly from the contact layer of that insulating material, causing a steep heat gradient in that layer. But perhaps this error may be insignificant.

It naturally pleased me that Mr. Randolph used the thermal ohm in giving his results; the example he sets is, in my opinion, a good one, and it is hoped will be generally followed.

The process which he uses is to generate the heat electrically and then measure in water that which escapes. That is just the reverse of what would seem to be the more rational method, because heat can be measured so much more accurately and more simply in the form of electrical energy. Water is one of the worst substances to use, because it has about the highest specific heat of all materials, hence it takes much heat to change the temperature very little. It is like finding the motion of the long end of a lever by measuring the movement of the small end.

It occurred to me that the method might perhaps be modified by placing a flat electrically-heated disk between two equal slabs of the insulating material to be tested; the heat, which could then easily be measured as electric energy, would then flow out thru both slabs in parallel. The same guard-ring device might then also be used.

MR. C. E. SKINNER: We have used apparatus quite similar to that described by the author for obtaining results of the same

general character. We have also made tests on this apparatus, arranged as suggested by Dr. Hering, *i. e.,* by having the source of energy in the center and the heat flowing both ways, duplicating the material on both sides and taking the average results thus obtained. We have found difficulty in repeating results to an accuracy that seemed satisfactory, even on the same class of material. We have had no difficulty in repeating results on the same sample, and we have therefore come to the conclusion that samples which seem to be quite the same may have considerable inherent differences. In our apparatus we use the equivalent of a guard-ring scheme, whereby we measure the heat-conducting power of material through which the heat flows at a direction normal to the surface, thereby in a large measure eliminating corrections.

We found that in using our apparatus the results were not consistent if the apparatus was placed in different positions, and this led to the arrangement of revolving the completed apparatus at a slow rate in order to get as nearly as possible uniform conditions, so far as convection currents and radiation effects to different parts of the room are concerned, and this has resulted in much more satisfactory work.

Mr. C. P. Randolph: I have also found that the direction of the heat flow varied considerably according to the resistivity of the material. I should also think that in the method suggested by Mr. Hering the trouble would be that while the general plan seems to be very good, you have to get almost the same total resistance on each side of the plate to get accurate results, and we have experienced difficulty in getting that.

Dr. Joseph W. Richards: In calculating the conductivity as outlined in the paper, I have found in the case of some of the materials tested that it was constant, that others fell off a little, and that only one material had conductivity proportional to the absolute temperature, as assumed by Mr. Hering in his theoretical paper on heat conductance, in this volume.

Mr. Randolph (*Communicated*): We consider it more accurate to measure the amount of heat that has actually flowed through the material, even though this method does require that a current of water be used. In order to measure the watts elec-

trically, it would be necessary to bury a flat heating unit in the mass of insulation and assume that the flow of heat through each side was proportional to the thickness, *i. e.*, to have the resistivity of the material on each side the same. The low temperature side should be cooled with water, as otherwise the heat flow will depend on the kind of surface from which the heat leaves the apparatus, the room temperature, kind of walls, etc., and cannot be controlled. The correction for side losses is also important, and requires the assumption of certain geometrical formulæ. It will be noticed that with the apparatus I have described it is very simple to change samples.

Like Mr. Skinner, we find that the results with certain materials vary with the direction of the flow of heat. We can duplicate results on different samples of the same material within a few percent in most cases, but in others we could not.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE VOLATILITY OF ZINC OXIDE.

By O. L. Kowalke.

Several years ago, in connection with some experiments on the electric smelting of zinc ores, the question arose whether zinc oxide was volatile or not. In the literature there seemed to be only general statements as to the temperatures at which zinc oxide was volatile, but no record of definite tests was found. Stahlschmidt[1] says: "Zinc oxide is infusible and is notably volatile at 970° C., and about 15 percent more at 1054° C., and is rapidly volatile at a high heat."

After the present investigation had been completed, it was found that this question had been studied by Messrs. Doeltz and Grauman.[2] Their methods are about the same as in this work, but the results are somewhat different, as will be explained later.

APPARATUS.

Pyrometer: A carefully standardized and properly protected thermocouple of platinum and platinum-10-percent-rhodium and a galvanometer of Keiser & Schmidt served as the means of determining the temperatures attained.

Zinc Oxide: The zinc oxide employed was "Zinc Oxide, C. P.," obtained from E. H. Sargent & Co., and was not tested for its purity.

Furnaces: The first furnace used was of the granular carbon resistor type. The treating chamber was a magnesia crucible 4¾ inches (12 cm.) long, 1¾ inches (4.3 cm.) in diameter, walls ¼ inch (0.6 cm.) thick, closed at one end, and surrounded by a shell of Acheson graphite. All of it was imbedded in the resistor in a horizontal position, with the opening of the crucible through the wall of the furnace. This arrangement allowed the introduction and removal of the zinc oxide from the furnace in a

[1] Ingall's "Metallurgy of Zinc and Calcium." p. 5.
[2] "Metallurgie," **1906**, 212, 233.

convenient manner. The mouth of the crucible was closed with a magnesia disk through which the pyrometer and sight tube were inserted, and the whole was cemented up with asbestos fibre.

This type of furnace was very convenient, but trouble lay in the fact that there was danger of reducing gases coming through the wall of the magnesia crucible. This did happen, and the results were of no value.

The only type of furnace that did not introduce any reducing material was a tube furnace of the Heraeus form, wound with some high melting-point metal, such as "nichrome" or platinum. Such a furnace consisted of a tube of porcelain or "Marquardtsche Masse," about 1 inch (2.5 cm.)in diameter and 10 inches (25 cm.) long. A spiral of resistance wire was on the tube and connected to the terminals at the ends of the furnace. The annular space of about 3 inches (7.5 cm.) between the tube and the casing of the furnace was filled with fossil flour to serve as heat insulator.

The electric current from a 110-volt circuit used for heating the spiral of resistance wire was regulated by means of a bank of incandescent lamps, which proved to be a convenient method for control of the current and hence of the temperature.

The "nichrome" ribbon does very well for temperatures below 1100° C., but temperatures above this can not be maintained very long, as the metal oxidizes rather rapidly. The platinum foil can, of course, be heated to a higher temperature, but in this case the foil was so thin that it was not safe to go above 1400° C. In this connection it might be of interest to state that a thin platinum foil does not work well with alternating current, as the vibrations resulting from this power break the foil. Direct current is entirely satisfactory.

PROCEDURE.

The zinc oxide was placed in a boat about 3/8 inch (0.9 cm.) wide, 3/8 inch (0.9 cm.) deep and 3½ inches (9 cm.) long. Before using a new boat or fresh zinc oxide for any test they were both first ignited in a Bunsen flame to a constant weight.

The boat with the weighed amount of zinc oxide was then put in the furnace, and the pyrometer so placed that the junction

of the couple was at the middle of the boat. The end through which the pyrometer was inserted was cemented up with loose asbestos, and the other end was provided with a tube about 3/8 inch (0.9 cm.) diameter, open at both ends, which served as a sight tube.

The furnace with its contents was now slowly heated to the temperature desired, kept there, and then finally allowed to cool slowly to the original temperature. The period of cooling was usually over night, after which the boat with its charge of zinc oxide was removed and weighed. The loss of weight was considered due to the voltilization of the zinc oxide. The weight of the porcelain boat was very constant, and any variations in its weight were applied to the apparent loss of zinc oxide.

RECORD OF TESTS.

With Resistor Furnace: Several runs were made with this furnace, but in all of them the zinc oxide apparently volatilized at temperatures below 1300° C. White fumes of zinc oxide were observed at the exit at temperatures varying from 1150° C. to 1240° C. in the several runs, and it will be noted that these are about the temperatures at which zinc oxide is reduced. There seemed to be no question that the carbon monoxide from the furnace came through the walls of the magnesia crucible and reduced the zinc oxide. These tests are thus of no value so far as this problem is concerned.

With Tube Furnace Heated by Metallic Ribbon: It was clear from the above tests that even a small amount of reducing agent must be kept out of the furnace. The tube furnace satisfies these conditions, and the results obtained are much more satisfactory. Below are given in tabulated form the results of the successful tests:

No. 1		No. 2		No. 3	
Time	Temperature Degrees Centigrade	Time	Temperature Degrees Centigrade	Time	Temperature Degrees Centigrade
9.00	635	3.30	910	11.00	1075
10.00	1165	3.44	1190	12.00	1260
11.30	1210	3.48	1260	2.00	1325
12.00	1240	3.50	1290	2.30	1360
				3.30	1370

	No. 1	No. 2	No. 3
Weight ZnO taken	1.0030 grams	0.7560 grams	0.9042 grams
Loss of ZnO	0.0102 "	0.0305 "	0.9040 "
Percent loss	1.01 "	4.3 "	100.0 "

DISCUSSION OF RESULTS.

It appears from these tests that zinc oxide can be completely volatilized at temperatures from 1370° C. to 1400° C. In all of these tests the zinc oxide was exposed to the high temperatures for a considerable period of time, a condition not exactly comparable to smelting conditions.

The loss of zinc oxide increases rapidly with temperature rising above 1300° C., as shown in these tests. The loss seems, however, to be of a nature similar to the slow evaporation of water below the boiling point, but at temperatures above 1400° C. it appears reasonable to say that the volatilization proceeds rapidly.

This view is supported by the work of Doeltz and Grauman, who find that at 1400° C. a series of nine treatments, for periods of 10 minutes each, produced a loss of 13 percent of zinc oxide. However, when zinc oxide was dropped on a platinum wire heated by a current of electricity to a bright red heat, the zinc oxide adhered tenaciously, and upon heating the wire to a white heat, above 1400° C., and near its melting point, a rapid volatilization of zinc oxide took place.

The painstaking assistance of Mr. Albert R. White in obtaining these data is hereby acknowledged.

Laboratory of Chemical Engineering,
University of Wisconsin.

DISCUSSION.

DR. JOSEPH W. RICHARDS: There has been a good deal of uncertainty as to whether zinc oxide itself was volatile at a moderate temperature or not, and this paper finally settles the question. If we had the complete vapor tension curve we could draw some further conclusions.

A paper presented at the Twenty-first General Meeting of the American Electrochemical Society in Boston, Mass., April 20, 1912, President W. R. Whitney in the Chair.

THE NATURE OF ZINC CEMENTIZING (SHERARDIZING).

By Arden R. Johnson, Ph. D., and Willis R. Woolrich, B. S.

It is now about a decade since Sherard Cowper-Coles made the discovery, quite by accident, that if a piece of metal, like iron, for example, is buried in zinc-dust, and the mass heated out of contact with air, there is deposited on the iron a beautiful coat of zinc. The process was given the trade name "Sherardizing," but a term more appropriate, in the light of the nature of the process, is "zinc cementizing," analogous to carbon cementizing of iron.

While the commercial application of the process appears to have been slow at first, it, nevertheless, grew steadily in favor for certain kinds of goods, and, after getting a firm hold in England, appears to be spreading rapidly in the United States.

The close attention which this process is attracting may be due largely to the simplicity of the process and to the mystery surrounding the actual nature of the deposition, but, as we believe, is due more largely to the very great value of the coating as a protective agent for iron and steel goods. Any process that brings engineers and chemists one step nearer the solution of this so important problem in the realm of the conservation of building materials must surely attract the most serious attention. With this fact in mind, we present some results gleaned from a rather broad industrial research on zinc cementizing, which we hope are of sufficient scientific value to be of general interest.

Fundamental Factors in the Process.

In working the process of "Sherardizing," whether for commercial or scientific ends, we must know the amount of zinc deposit as a function of the following factors: Temperature, time, concentration of zinc-dust in inert powder, and size of zinc

particles. No doubt, much of such information has been obtained, but it does not appear to have been published as definite data.

To study the effects of the above-mentioned factors, we first used a small apparatus modeled after the commercial apparatus. A piece of 2-inch (5 cm.) gas pipe about 8 inches (20 cm.) long

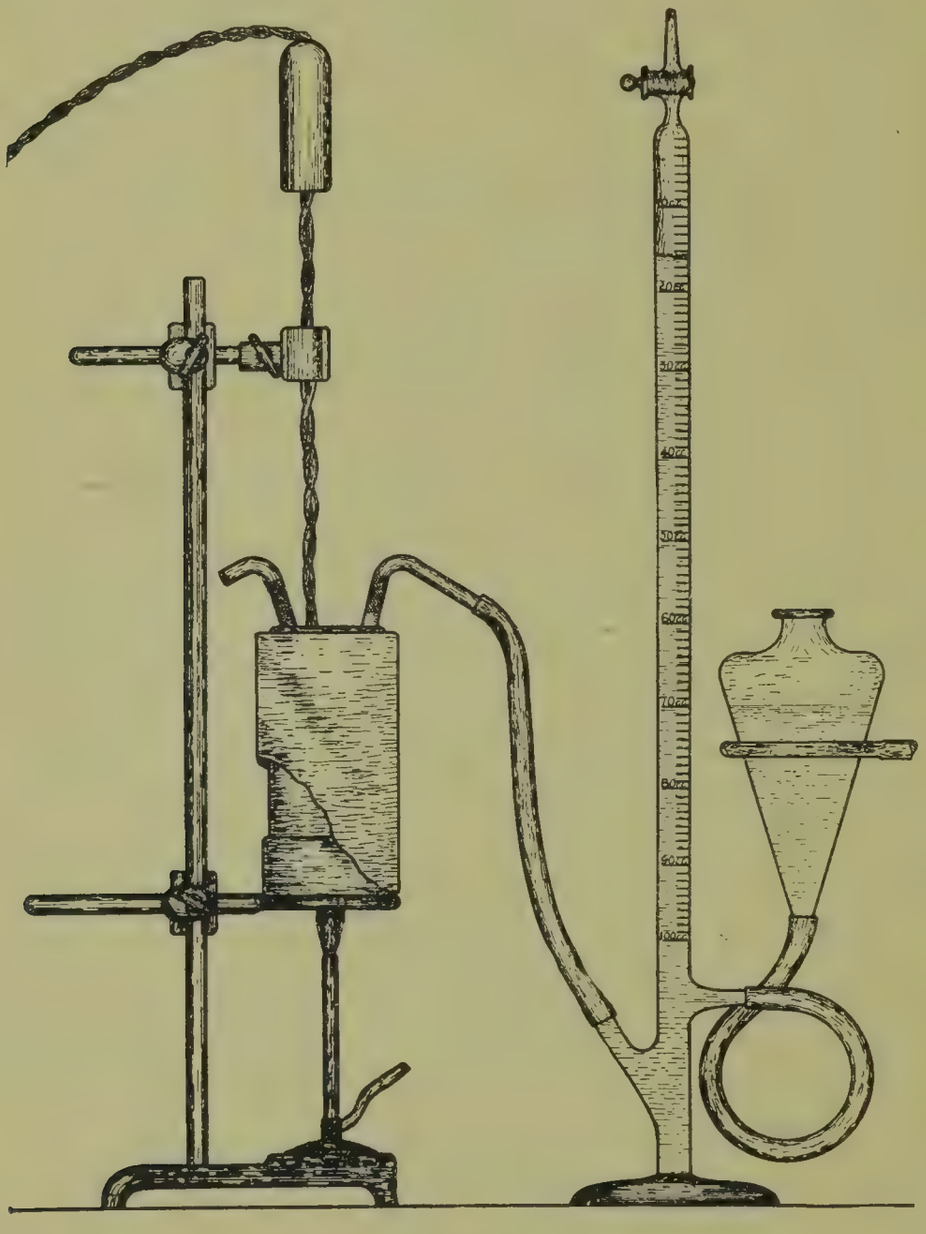


FIG. 1.

had fitted to each end a cap. One of these caps had a 3/8-inch (1 cm.) hole bored at its center thru which a thermometer could be inserted along the axis of the pipe. The other cap had drilled in it ten holes of $\frac{3}{16}$-inch (0.5 cm.) diameter. This tube was filled with zinc-dust, or mixture, and placed horizontally in an asbestos-lined iron box heated from below by Bunsen burners. Samples to be "Sherardized" were pieces of No. 9 wire, such

as is used for wire nails, about 8 inches (20 cm.) long. When the temperature of the zinc-dust was brought to the desired value, the iron wire samples could be inserted into the zinc-dust or withdrawn *ad libitum* thru the holes in the cap. This apparatus, tho to all outward appearances a well-working machine, gave too erratic results for scientific ends, so another design was

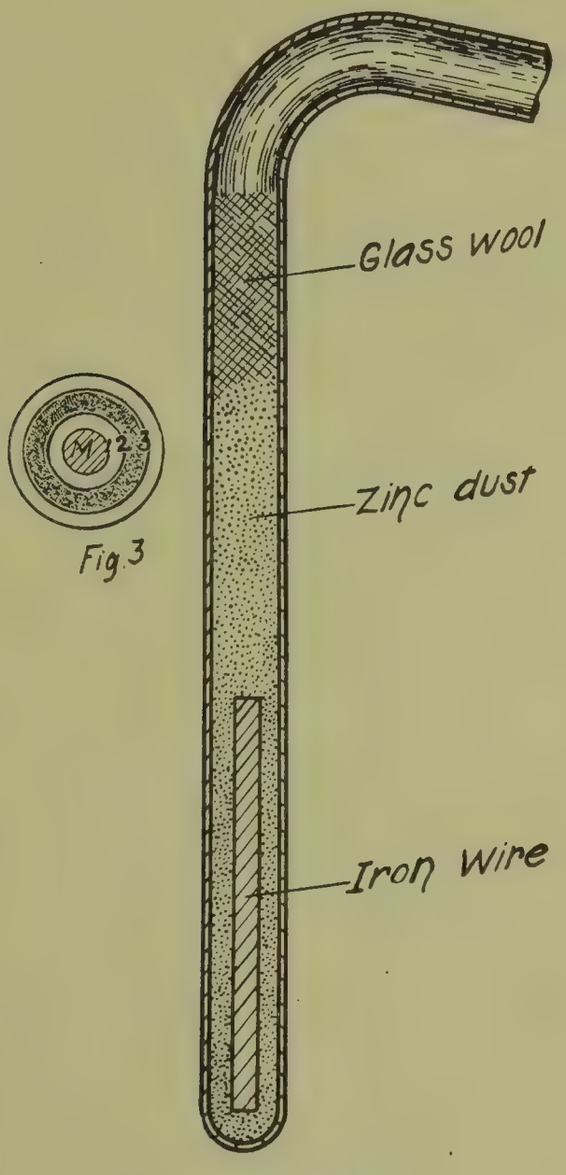


FIG. 2 (inc. FIG. 3).

gotten up which worked very successfully, and is shown in Fig. 1.

A similar piece of gas pipe, provided with a cap at one end, served as a container for $NaNO_3$, or a mixture of $NaNO_3$ and KNO_3 kept in a state of fusion at some particular temperature by a Bunsen burner. To prevent excessive radiation, this vessel was surrounded by an asbestos jacket. The couple of a Hoskins' pyrometer was placed in the bath as shown. With this apparatus

it was found feasible to maintain any temperature from 250° C. to 500° C., within limits of five degrees.

The sample of metal to be "Sherardized" was usually 75 mm. long and a little over 3 mm. in diameter (size of No. 9 wire). This sample, after being pickled, sandpapered and polished, was placed in a glass tube of about 7 mm. internal diameter, as shown in Fig. 2, and the zinc-dust, or mixture of zinc-dust and inert powder, filled in around the sample and to a considerable depth above the top of the same. A layer of glass-wool was next stuffed into the tube and gently pressed down upon the zinc-dust. The top of the tube was then heated in the Bunsen flame and given a gentle bend to a little less than a right angle with the main portion of the tube, so that the tube with its contents could be immersed in the bath with the upper end hooked over the edge of the vessel. The bend also prevented the expulsion of the glass-wool wad when the gases begin to come off rapidly from the highly heated powders. Part of the glass-wool fibers became fused to the wall of the glass tube. With the apparatus shown in Fig. 1 a dozen tubes could be hung in the bath at one heating. The gases evolved could also be collected by connecting a nitrometer with one of the tubes as shown.

Determination of Zinc Deposited Per Sq. Cm. of Surface.

The most essential and critical point to be determined under a specified set of conditions is the weight of the zinc deposit per sq. cm. Two methods were used:

(1) The determination of the increase in weight of the sample by weighing it before and after the run.

(2) Measuring the amount of hydrogen evolved from the sample by the action of HCl on the zinc coat.

For carrying out the latter method a gas burette, provided with facilities for making corrections for both temperature and pressure (described in Hempel's *Gas Analysis,* p. 73), was connected with a glass-stoppered test-tube thru a side-tube on the latter. The test-tube was nearly filled with a hydrochloric acid solution made by diluting one part of hydrochloric acid (*e. g.*, 1.21) with seven parts of water. Such a mixture was found to attack iron relatively slowly.

RESULTS WITH PURE ZINC-DUST.

Our first studies of "Sherardizing" were made with the purest grade of zinc-dust obtainable. The material was impalpably fine, and, under a magnification of 600 diameters, appeared to be perfectly amorphous.

Relation of Duration of Heating to Thickness of Deposit.

Several glass tubes were provided with samples of iron in the manner already described, and each one covered with approximately the same amount of zinc-dust. The material was shaken down around the specimen by gently tapping the glass tubes on the table until there was no further appreciable settling. After carefully regulating the fused sodium nitrate bath to a certain temperature the tubes were immersed in it and maintained at constant temperature, each sample for a specified time. They were then removed, one by one, at regular intervals, allowed to cool, broken open, and, after the loose zinc-dust was wiped off with a cloth, the value of the zinc deposit was determined by one or both of the methods described.

The results of some runs are shown by the curves on Plate I. Curve No. 1 was obtained for polished iron at a temperature of 375° C. It is apparent that the deposition of zinc is very rapid in the first hour. After that, however, the rate is slower, and almost proportional to the time for several hours. This holds true for pure zinc-dust without admixture with an inert powder. As the first part of the curve is particularly interesting, this was studied to greater detail by preparing six samples of iron in tubes, as described, and fastening them in an asbestos holder so that they could all be immersed simultaneously in the bath, but removed singly. In the course of the heating, one tube was removed every ten minutes. Curve No. 2 expresses the results obtained by such a procedure at 420° C. It is interesting to note how rapidly and promptly the deposition starts. Also, a comparison of the curves for the first hour at 375° with the one at 420° shows how much the higher temperature enhances the rapidity of the process.

Curve No. 3 was obtained for the same sort of iron samples as used before, excepting that they were not pickled and polished,

but left as they were—covered very uniformly with a thin film of oxide. A comparison of the curve for these rusty samples with Curve No. 1 shows what a great hindrance even a very thin coat of rust is. In fact, there was as much zinc deposited on No. 1 in one hour as on No. 2 in six and one-half hours.

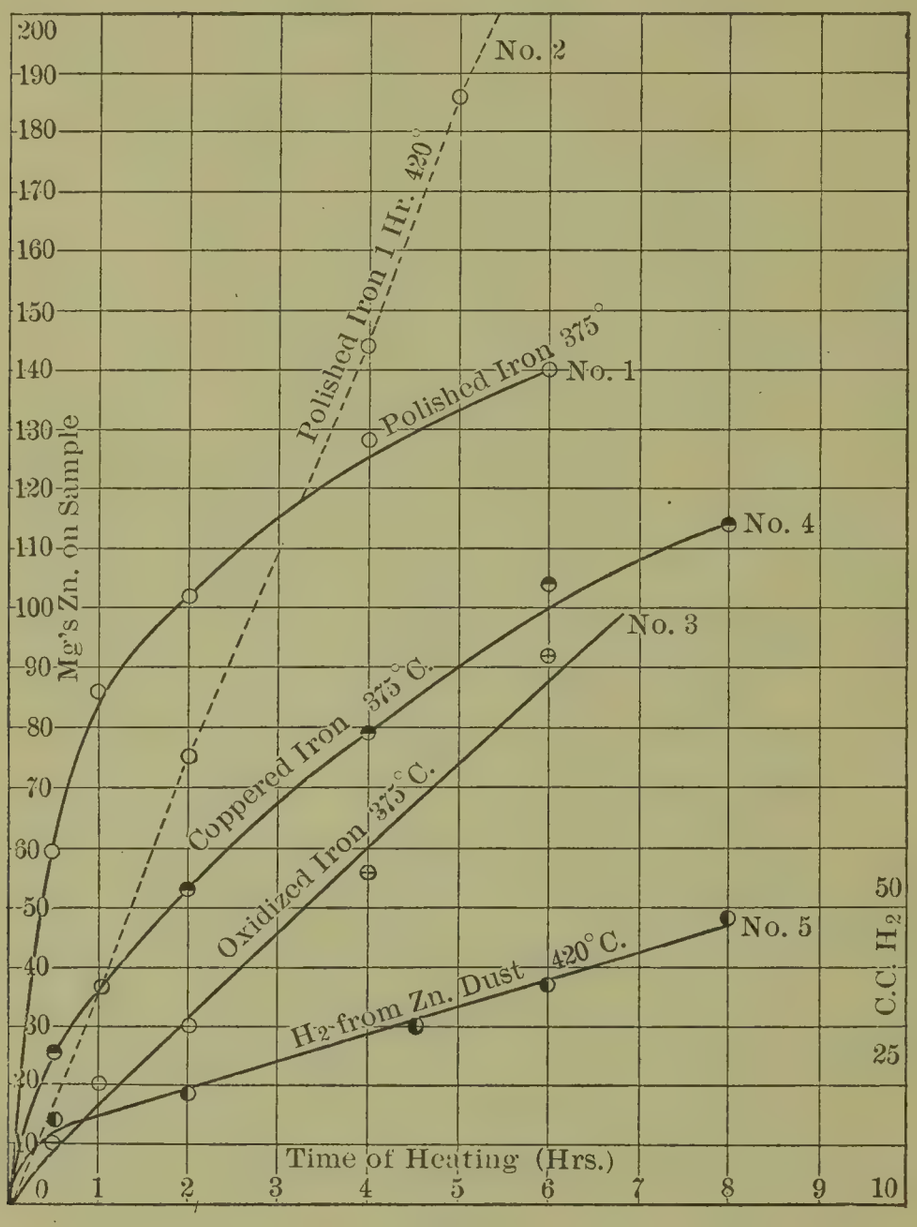


PLATE I.

Early preliminary experimentation had shown the great readiness with which copper "Sherardizes," so a piece of iron was given a thin coat of copper and then "Sherardized" at different temperatures. Curve No. 4 would appear to show that nothing can be gained by such a procedure, tho, of course, the possibilities along this line were not by any means exhausted.

Evolution of Hydrogen from Zinc-dust.

It is a well-known fact that practically all very finely-divided materials absorb and retain considerable quantities of moisture. This is notably true also of zinc-dust. With our apparatus disposed as shown in Fig. 1 we found that a very considerable volume of gas was evolved during the Sherardizing process. Curve No. 5 is a typical one, taken while "Sherardizing" samples of iron at 420° C. A qualitative examination of the gas proved it to be almost pure hydrogen, with, of course, some air. A sample of the purest zinc-dust gives up about 7 to 8 c.c. per gram, in six hours, at a temperature of 420°. This fact is

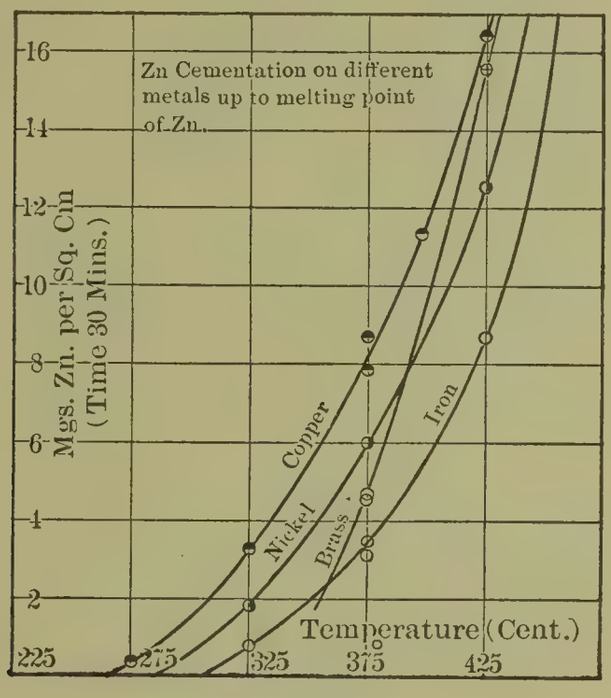


PLATE II.

quite significant, for there is thus provided a reducing atmosphere in the interstices or voids that exist in the zinc-dust surrounding the iron.

Effect of Temperature upon Rate of Deposition of Zinc.

As in most physical and chemical processes, so in the case of "Sherardizing" metals, the temperature factor is of extreme importance, and therefore many carefully arranged experiments were carried out to determine the rate of deposition of zinc not only upon iron, but also upon nickel, brass, copper and zinc. Plate II shows typical curves representing the results obtained

under proper conditions. Evidence is clear that not all metals, even those much less electropositive than zinc, "Sherardize" with the same degree of readiness. Copper, as might be surmised, receives a coat of zinc much more readily than the other metals. The authors have produced coats on copper ranging from a mere film of yellow brass to a pure white of remarkable smoothness. Pure nickel "Sherardizes" more readily than iron. A rod of pure zinc, polished until perfectly smooth, did not start to "Sherardize" to any considerable extent until a few degrees below its melting point. Yellow brass receives a coat readily, but not so readily as does copper, and the curve has a somewhat different trend. But of greatest interest is the fact that all the curves approach the same rate of deposition with rise of temperature, and the limiting value lies at about the melting point of zinc. From this point on, the deposition of zinc becomes exceedingly rapid. The range of temperature between the point where the first appreciable deposit occurs to the melting point of zinc may be looked upon as the true "Sherardizing" range of temperature for a particular metal. This range is greater for copper than for iron.

Effect of State of Division of Zinc.

One of the most surprising facts which we have come upon in our study of zinc cementizing is the pronounced effect the fineness of the zinc particles has on the rate of deposition and smoothness of the zinc coat. The finer the zinc particles the smoother and apparently more penetrating the zinc coat. But the finest of zinc-dust will not deposit as fast at a particular temperature as a relatively coarse zinc-dust of 150 to 100-mesh. Results were obtained which showed nearly twice as rapid a deposition of zinc at 370° C., in three hours, from 150 to 100-mesh zinc, than from the finest zinc-dust. The coat is quite rough for the coarser dust, however. For commercial work, one might strike a proper medium between smooth, penetrating coats, slowly deposited, on the one hand, and rough, thick coats, quickly deposited, on the other. Coarse zinc-dust is much less satisfactory in other respects when used alone than fine zinc-dust, for it yields but little hydrogen when heated, and the voids are so large as to allow air to penetrate the mass to considerable depths and oxidize both

the sample receiving a coat and the particles of zinc, often to such an extent as to destroy the "Sherardizing." Besides, there is a great tendency for the coarser material to fuse together. It is therefore necessary to use some impalpably fine, inert powder with such so-called "finely-divided zinc," to at least partly fill the voids.

Zinc-dust with Inert Powders.

The curves on Plate III are plotted for results obtained with bauxite, barium sulfate and powdered quartz mixed in different proportions by weight with zinc-dust. These powders were exceedingly fine, and, before being mixed with zinc, were heated

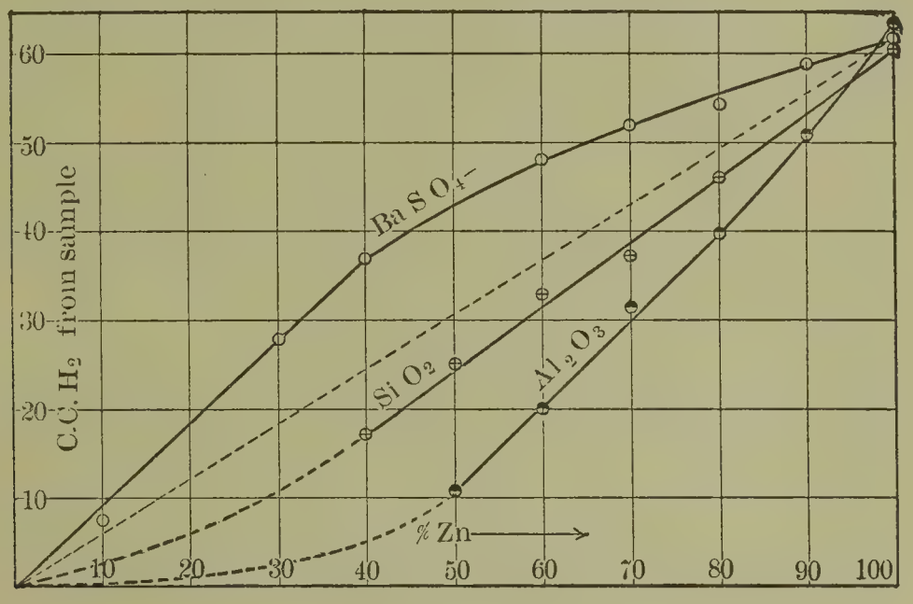


PLATE III.

to 500° C. for some time to drive off moisture. With barium sulfate the deposition of zinc falls off slowly, while with quartz and bauxite the deposition falls rapidly. Reasons for these different effects are found partly in the fact that the latter powders are much more voluminous than barium sulfate, and also appear to "cake" quite readily with the lower percentages of zinc. If a powder like barium sulfate is mixed with zinc-dust by volume instead of by weight, the deposition is about proportional to the zinc content, as shown by the dotted line.

A rather surprising fact presented itself when we opened several glass tubes containing samples which had been charged with mixtures of zinc-dust and bauxite, or zinc-dust and quartz, and heated several hours. As the percentage of inert powder is

increased there is a greater and greater tendency for the contents of the tube to cake. Up to 40 percent of inert powder this congealing is not sufficient to exert much influence on the process, but greater percentages interfere with the deposition of the zinc. The contents of several tubes with only about 10, 20 and 30 percent of inert powder, heated at 385° C. for four hours, were just sufficiently caked to barely hang together. It was noticed that immediately next to the iron sample there was a zone of considerable thickness of pure white powder; then around this another zone which was composed of zinc-dust and inert powder like the original mixture. It was also very noticeable that the demarkation between the white zone and the residual zinc-dust mixture zone was very sharply defined. Further examination under a powerful microscope revealed the fact that there was hardly a particle of zinc remaining in the white zone, and that the surface of demarkation between the two zones was really remarkably defined. The thickness of the white zone varied, of course, with the duration of run, temperature and concentration of zinc-dust mixture.

Fig. 3 represents a cross-section of the system after being heated. *M* is the iron wire sample, *1-2* is the white, pure, inert powder zone depleted of zinc-dust, *2-3* is the zone of zinc-dust and inert powder of original composition, *1* is the deposited zinc coat on the iron, *2* is the surface of demarkation between the zones described.

Theory of Zinc Cementizing ("Sherardizing").

We regard the above-described experimental facts of value in determining the nature of zinc deposition in the "Sherardizing" process. Our explanation or theory of the process is as follows: In the light of the phase-rule we may regard the iron, zinc and vapor as forming a closed system, all parts of which are practically at the same temperature. Zinc, compared with iron and most other metals, has a relatively high vapor tension. Zinc alloys fairly readily with many of the common metals like iron, nickel and copper. When the process is ready to be started, the iron, for instance, is surrounded and in intimate contact with many particles of zinc. Under the influence of heat these particles, carrying their slight atmospheres of zinc vapor, form a

superficial alloy with iron. This superficial alloy on the iron would very likely be a solid solution of zinc very rich in iron. Now we may look upon the iron with its insignificant vapor pressure as greatly lowering the very appreciable vapor pressure of the zinc which is forming a solid solution with it, and we should expect the zinc vapor to distil from the points of higher tension to the place of low vapor tension at the surface of the iron-zinc alloy. As the iron alloy grows richer and richer in zinc under the process of sublimation or distillation, its vapor tension will gradually approach the tension of the vapor of pure zinc particles, and hence the process gradually ceases.

The experimental facts already presented show that the nature of the metal to be "Sherardized," having reference to its alloying properties with zinc, has a great influence on the temperature at which "Sherardizing" will start and its rapidity after starting. That we did not succeed after several trials in depositing zinc on a pure zinc rod buried in zinc-dust is also in accord with our theory. Also, pieces of iron which had once received a coat of zinc of considerable thickness refused to "Sherardize" at any such rate as fresh iron at temperatures below the melting point of zinc. However, if the coat of zinc already present is thin, the deposition will start again, tho more or less tardily.

New lines for experimentation are suggested by this theory which should at the same time test its validity. We should expect zinc cementizing to be greatly retarded if the finely-divided zinc used were a solid solution with some metal of low vapor tension, as iron, nickel or copper. If the vapor tension of the metal to be deposited is lowered until about equal to that of the most saturated solution possible on the surface of the metal being "Sherardized," the process should not take place, or only to a slight extent. Furthermore, any substance which would impair or change the initial alloying tendencies of the metals should also greatly influence the process. It is along these lines that the authors are now proceeding in their experimentation.

De Paul University,
Chicago, Ill.,
February 12, 1912.

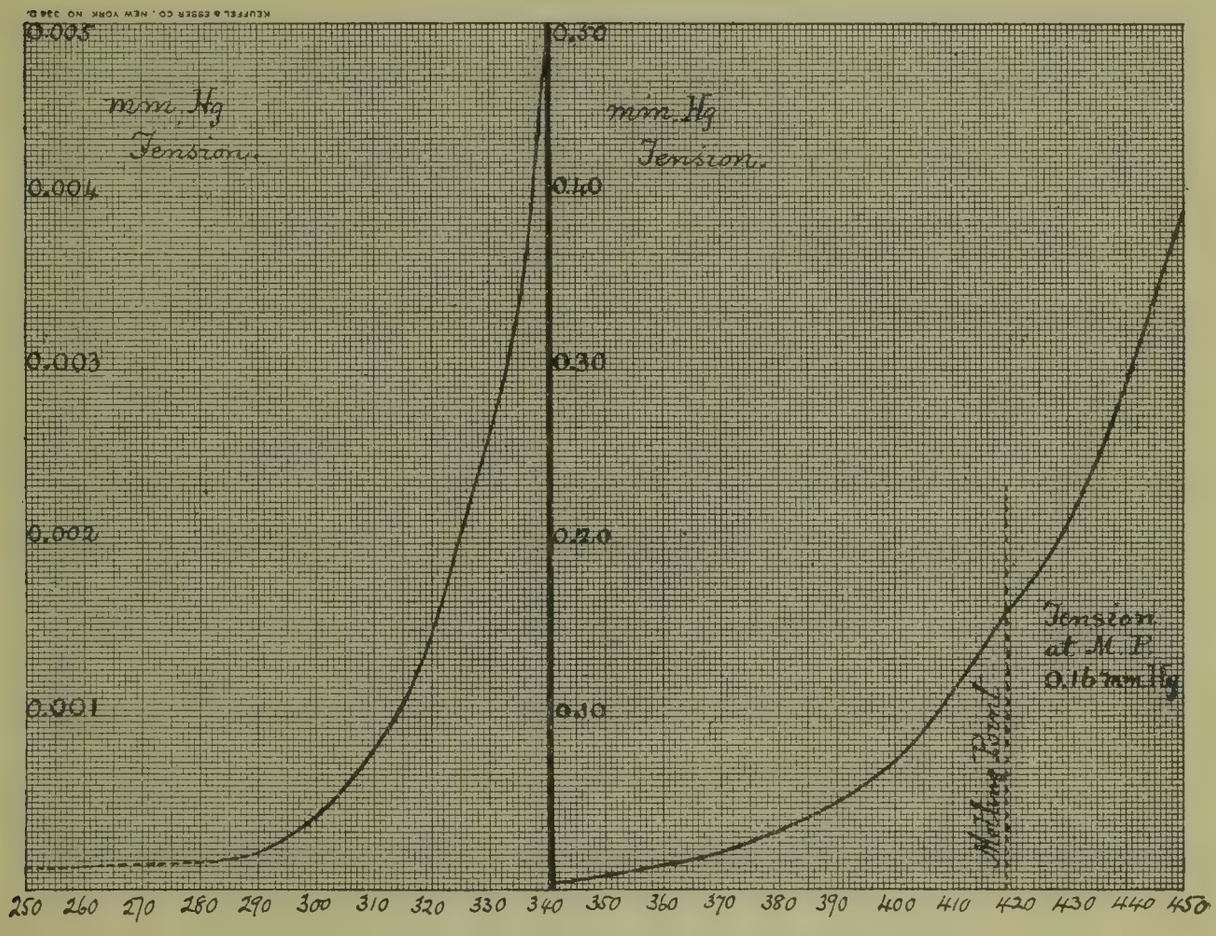
DISCUSSION.

PROF. C. F. BURGESS: The results which the authors give are not strictly applicable to the process in practice, owing to the fact that the experiments were conducted in a quiet mass, whereas ordinary Sherardizing processes are carried out in rotating drums, where there is mechanical abrasion. This has a decided influence on the rate of deposition of the zinc from the powder.

MR. ARTHUR: It may be proper at this time to call the attention of the meeting to the previous theories on this subject. The earliest theories, as you may know, were the vapor compression theory, and last year a paper was read before the Faraday Society, in which the author attempted to say that the process of Sherardizing was due to the contact of the zinc and metal. This paper presented this morning confirms the earlier theories which were held regarding Sherardizing, in so far as it shows that Sherardizing was accounted for solely on the vapor pressure. Some experiments which I have carried out during the last year prove almost conclusively that the Sherardizing process is due to the vapor pressures and not to the contact of the zinc on the iron.

DR. JOS. W. RICHARDS (*Communicated*): Sherardizing is an intensely interesting process, based on clear cut but not very generally understood scientific principles. As proved in the paper, coating with zinc takes place regularly below the melting point of zinc, with probably no distinct break at the melting point, as long as the zinc dust does not run together to fluid zinc The process is without doubt operated by the vapor-tension of the zinc, on the one hand, and the ability of the other metal, iron, copper, nickel or brass, to absorb zinc vapor, on the other hand. The process depends on "a push and a pull," the tendency of the zinc to vaporize and the tendency of the other metal to absorb the vapor. In the absence of numerical values for the heat of combination of zinc vapor with iron, copper, nickel or brass, to form alloys—the pull—I have reproduced in the adjoining diagram the probable vapor tension of zinc at low temperatures, derived by analogy from the vapor tension of mercury at low temperatures, as printed in my "Metallurgical Calculations,

Part III." While the figures given are not experimental results, yet they are worthy of consideration as first approximations. Johnson and Woolrich's results, as given in their Plate II, show that at a given temperature different metals absorb zinc vapor with different velocities; also that a given metal, at different temperatures, absorbs zinc vapor with different velocities. The first information tells us that Sherardizing depends partly on the specific attraction of the metal being plated for zinc vapor,



Vapor Tension of Zinc. Abscissas temperatures C°. Ordinates tensions in mm. of mercury (two scales).

the second makes it a probable assumption that it also depends upon the specific ability of the zinc dust to produce zinc vapor at the different temperatures.

As to the latter point, the vapor tension curve of zinc gives us interesting conclusions. Johnson and Woolrich made 30-minute tests with copper, nickel and iron, at 325°, 375° and 425° C. They give the weights of zinc absorbed at these temperatures, and we can compare these with the vapor tensions of zinc at the same temperatures, as follows:

Temperature °C	Tension of Zinc Vapor mm. Hg.	Relative Tensions	Square Roots of Relative Tensions	Relative Deposits		
				Copper	Nickel	Iron
325°	0.002	1	1	1	1	1
375°	0.028	14	3.7	2.4	3	4
425°	0.183	92	9.5	4.8	6.3	10.9

The fourth column is added because it would appear *a priori,* that if the tension of zinc vapor was zero at the absorbing surface, the driving force causing diffusion of the zinc vapor would be the maximum possible tension at the vaporizing surface, and the quantity of zinc diffusing, being proportional to the diffusion velocity, would then be proportional to the square roots of those maximum tensions. It appears that the agreement is not bad; in fact, in the case of iron is quite instructive. We would expect some deviations, because of the other variable factors entering into the question.

After the immediate surface of the metal becames coated, the absorbing power must rapidly decrease, and the rate of absorption would then be limited by the rate at which the zinc soaks in, or is transmitted inward, from the surface. It appears from Johnson and Woolrich's results, that while copper and nickel have a greater combining power than iron, as far as their immediate surfaces are concerned, that they do not, however, maintain that rate when greater quantities of zinc are absorbed at a higher temperature; the iron is evidently relatively more permeable to further absorption of zinc vapor, at the higher temperatures.

There is a rich field of study and research ahead of us, in the consideration of the vapor tension of the elements at low temperatures, below their melting points, and its application to explaining some present industrial processes and probably in developing some new ones.

Lehigh University,
April 15, 1912.

Dr. W. Lash Miller: I would like to ask whether Prof. Richards took that square root before or after he had the values

given as 0.8, 3, and 8.5. I do not see much reason for having the square root.

DR. RICHARDS: I first obtained the vapor tensions, and then thought that the square root of these should represent the velocity at which the zinc would travel.

PROF. W. D. BANCROFT: It is quite possible that one ought to take the square root of the pressure, but I really wish Mr. Richards would tell us how he worked that out in his mind, because it is not obvious to me why the rate would be proportional to the square root of the pressure, and I doubt its being so.

DR. RICHARDS: I considered the pressure of the zinc vapor as a driving force, similar to the pressure which produces the velocity of an air blast. In the latter case we know that $V = \sqrt{2\,g\,h}$, that is, the velocity which the air acquires is proportional to the square root of the pressure driving it, and I saw no reason why the same relation should not hold for zinc vapor. At the surface of the zinc dust the vapor has its maximum tension for the given temperature; at the surface of the article being treated the absorption of zinc reduces that tension, possibly to nearly zero, at least at the beginning of the operation, and the driving force to send zinc from the surface of the zinc dust to the surface of the article under treatment is at first the maximum tension of the zinc, and later some tension less than that, as the article becomes superficially saturated with zinc. Since the experiments I have been discussing were short-period experiments, lasting only 30 minutes, it is likely that the vapor tension of zinc at the surface of the articles under treatment was nearly zero, because of the rapid absorption of zinc by the article, and in that case the driving force would be nearly the maximum tension of the zinc at the surface of the zinc dust. Then the velocity of flow of the vapor would be nearly proportional to the square root of the maximum tension.

MR. L. H. DUSCHAK: I would like to ask Professor Richards whether the vapor pressure used in his calculation is that of the metal in large masses? It is well known that the vapor pressure of a liquid in very small drops is greater than when it is in large drops, and the same thing has been shown to be true of

very finely divided crystalline solids. It is therefore very probable that the zinc powder used in the Sherardizing process has a considerably higher vapor pressure than the ordinary metal.

DR. RICHARDS: I caulculated the vapor pressure from analogy with the mercury vapor pressure for large masses of mercury.

PRESIDENT WHITNEY: I do not know whether it is published or not, but it is known that there are different pressures for the different forms of zinc.

DR. RICHARDS: I took into consideration that the vapor tension solid is different from that of liquid, and continued the curve below 300° by comparison with solid ice. The comparison otherwise is between liquid mercury and solid zinc.

MESSRS. JOHNSON AND WOOLRICH (*Communicated*): The deposition of zinc upon a metal by heating the latter in powdered zinc may not be exactly the same in nature when working below and above the melting point of the zinc. We have shown that there is a very great change in the rate, if not the nature of the process, at the melting point of zinc, hence it may clarify the discussion to consider the two stages of the process.

We believe we have shown conclusively the nature of *true* "Sherardizing," *i. e.*, deposition of zinc, at temperatures below the melting point of zinc. Above the melting point of zinc the same features of the process are at work, but increased in intensity; and superimposed upon these factors are those due to actual contact of melted particles of zinc and the surface receiving the coat. Parallel to the nature of true "Sherardizing" we may have some such phenomenon as this occurring: A particle of molten, pure zinc comes in contact with iron, for instance. Through their alloying tendencies the zinc soon coalesces with the iron, probably the whole particle merging all at once with the iron. If the particle of zinc is at the incipient melting stage when it comes in contact with the iron and takes up a minute trace of the same, this trace of iron will immediately lower the melting point of the zinc, and hence the sudden fusing and spreading of the zinc on the iron surface it touches.

In reply to Prof. Burgess's comment that the conditions under which we investigated the nature of the process, namely, in quiet

mass, are not the same as those prevailing in commercial work where the whole mass is rotated, and hence abrasion, etc., do not play a part, we have this to say:

Actual abrasion of iron goods rotating in soft, impalpably fine zinc dust can amount to exceedingly little. The agitation might increase the rate of deposition to some extent, but not change the nature of the process. At and above the melting point of the powdered zinc the increased contact due to rotating the mass would greatly increase the rate but not the nature of the process as already explained for temperatures near and above the melting point of zinc.

In order to test our theory, as suggested in the last paragraph of our paper, we have recently used several series of zinc alloys—Zinc-Aluminum; Zinc-Tin; Zinc-Iron ($FeZn_{10}$) and others.

In all these the percent of metal added to Zn was small. Then, by a process which we have recently invented, these alloys were reduced to impalpable powders. Comparison of the rates of deposition of coats on iron or copper from these alloys shows that in not a single case is the deposition nearly as great as for pure zinc prepared and used under identical conditions.

We may further add these experimental facts:

Below the melting point of alloy nothing but pure zinc is deposited on the iron or copper. Thin strips of pure copper were "Sherardized" in $FeZn_{10}$ for 8 to 10 hours at about 380°-400° C. Under these conditions the zinc had completely soaked through the copper, yielding very brittle, crystalline and silver-white products. *Not a trace of iron was found in a single instance.* But when we work at temperatures higher and higher above the melting point of zinc we find iron (or other metal used in alloy) in increasing quantities in the coat. At higher temperatures the coat is also very crystalline and rough.

Thus far we have obtained no experimental results, nor observed any results obtained under commercial conditions, that do not accord with our theory.

We wish to thank Prof. J. W. Richards for his discussion of our paper. He gives us another view-point which will aid us greatly in keeping our experimentation on a sound, scientific basis.

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Increase in oxygen percent .	unit	98	222.6	unit	61	108
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*Figures cited from the respective papers: "Acetylene Welding," read by J. M. Morehead before the N. Y. Railroad Club, and "The Influence of Impurities in Oxygen When Used for Cutting Iron and Steel," read by Alex. E. Tucker before the Birmingham Section of the Society of Chemical Industry.

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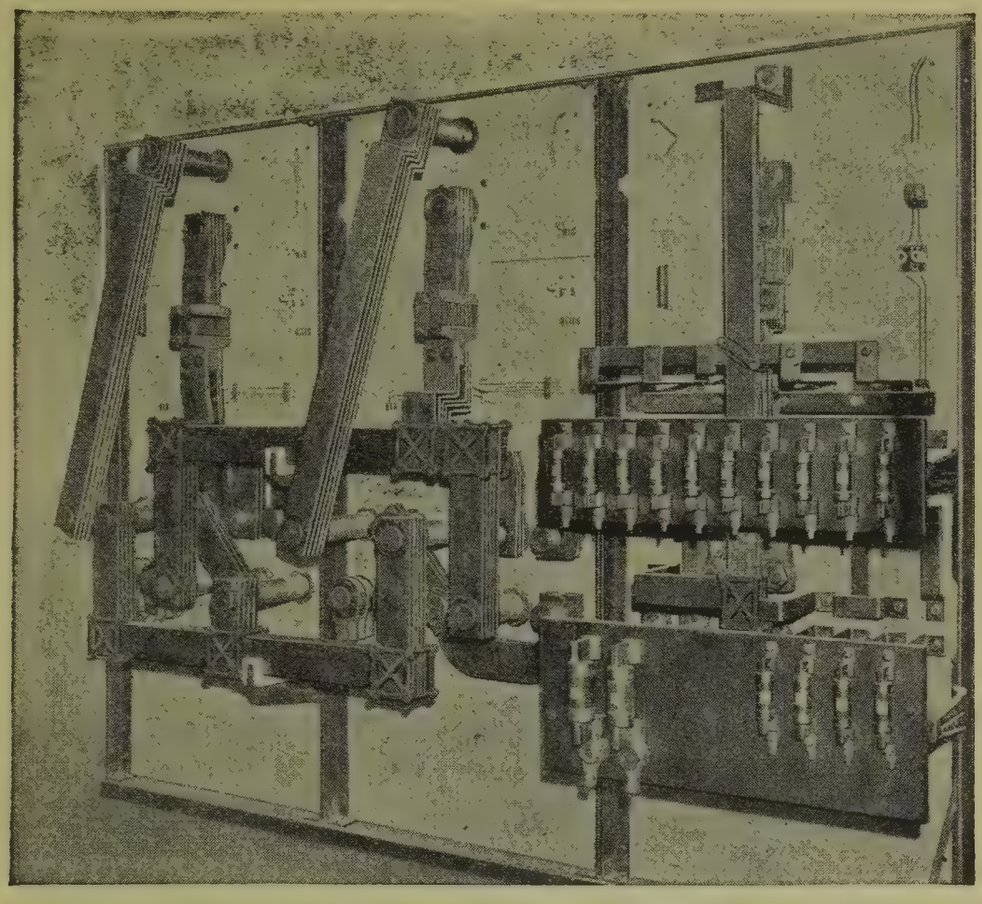

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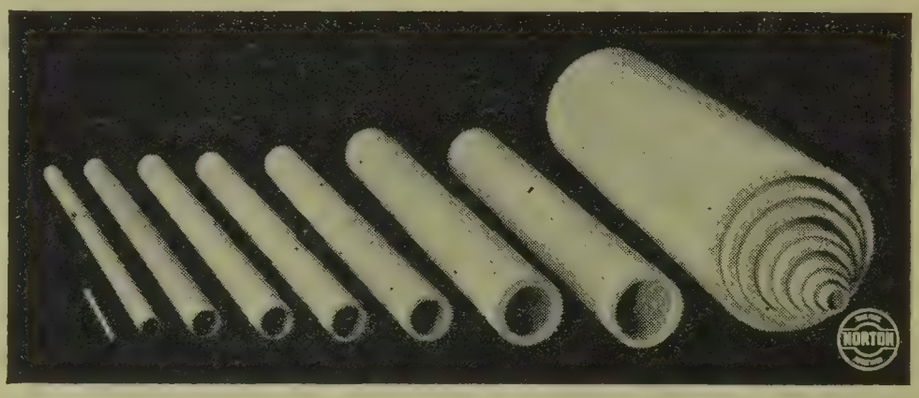

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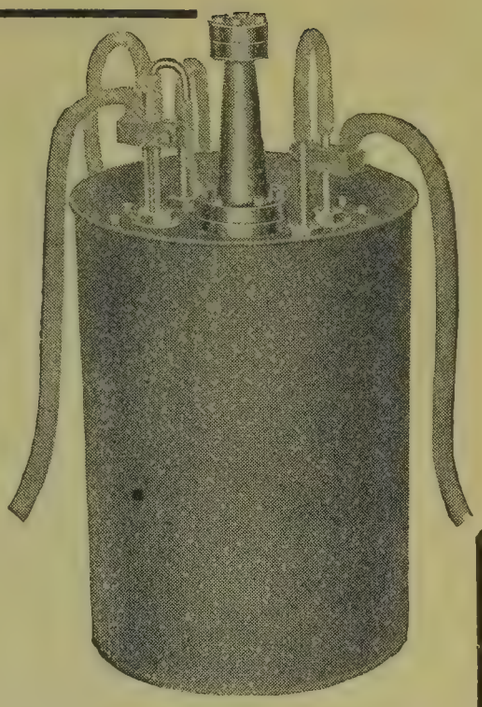

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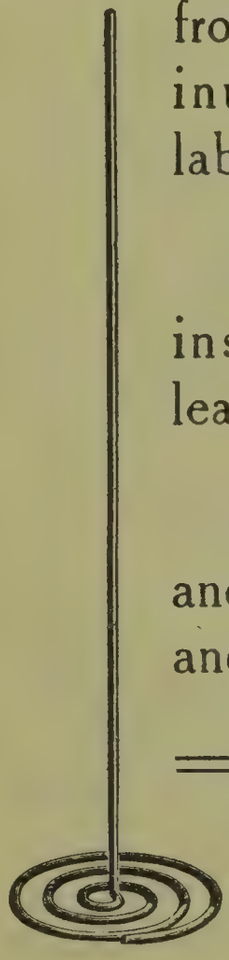

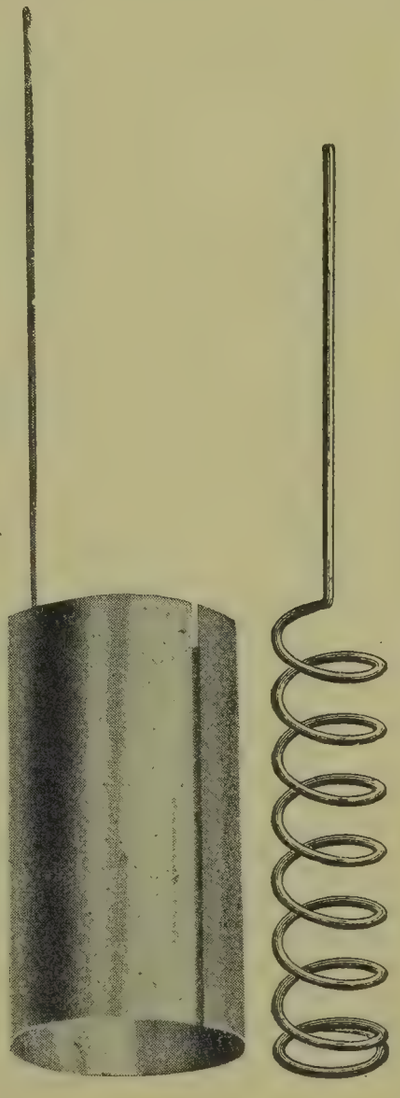

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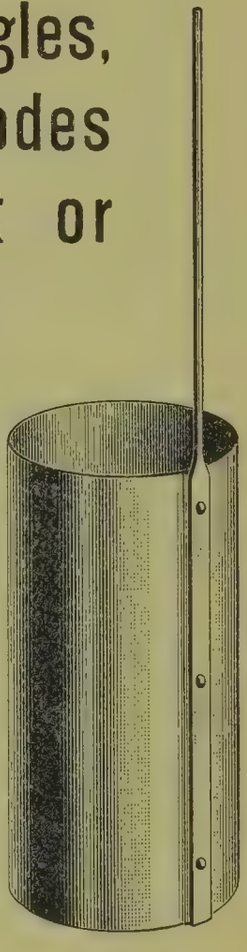

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IF YOU have not yet tried our Carbonless Ferro-Titanium as a purifying and deoxidizing agent you have missed trying the most effective cleansing agent for iron and steel in the Titanium alloy line which has thus far been produced. It is not only more effective than the alloy containing carbon, but also more economical to use.

We could write pages on the advantages of the carbonless alloy, but have found from experience that the simplest and easiest way to convince interested parties is to get them to try it. Once our material is given a trial, it sells itself.

Write for our pamphlet No. 20-X, containing full information regarding the alloy, and for a sample. Both will be furnished promptly on request.

Chromium and Manganese

These metals are produced 97-98% pure by the Thermit process and are entirely free from carbon. It is possible, therefore, to add as much or as little of them as may be desired to molten steel without danger of increasing the carbon content.

Manganese Alloys for Deoxidizing Brass and Bronze

For this purpose we supply Manganese Copper 30-70 and Manganese Titanium 30-35% Ti. These alloys are not only free from carbon, but also technically free from iron and are of the same high quality as the other metals and alloys which we produce and which can be had from no other source. As deoxidizing agents for brass and bronze they have no superiors on the market.

Write for our new pamphlet No. 20-X, on metals free from carbon, which gives full information regarding the alloys mentioned above, and also on our Ferro-Vanadium, Ferro-Boron, Ferro-Molybdenum, Manganese-Tin, Manganese-Zinc, Chromium-Copper and many other metals and alloys.

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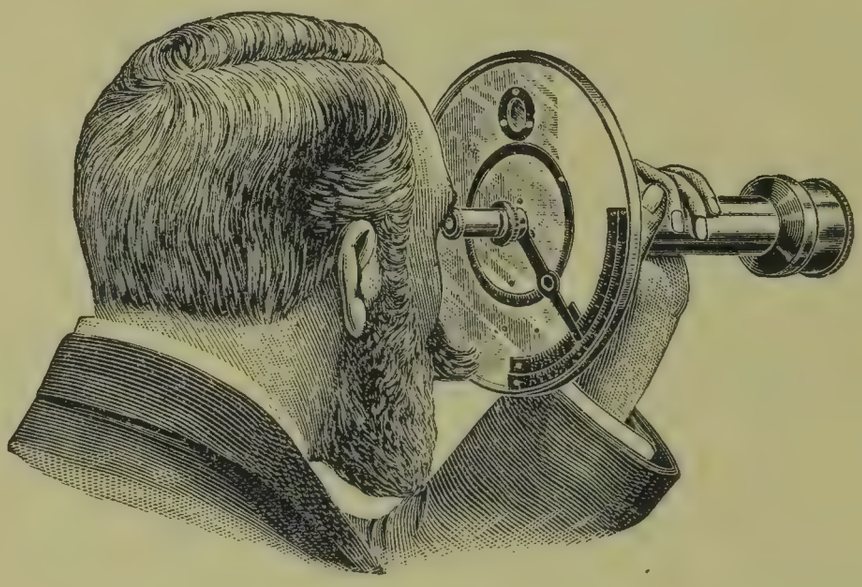

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